Development of an Improved Agricultural-Based Deicing Product

National Concrete Pavement Technology Center

Tech Center

Final Report
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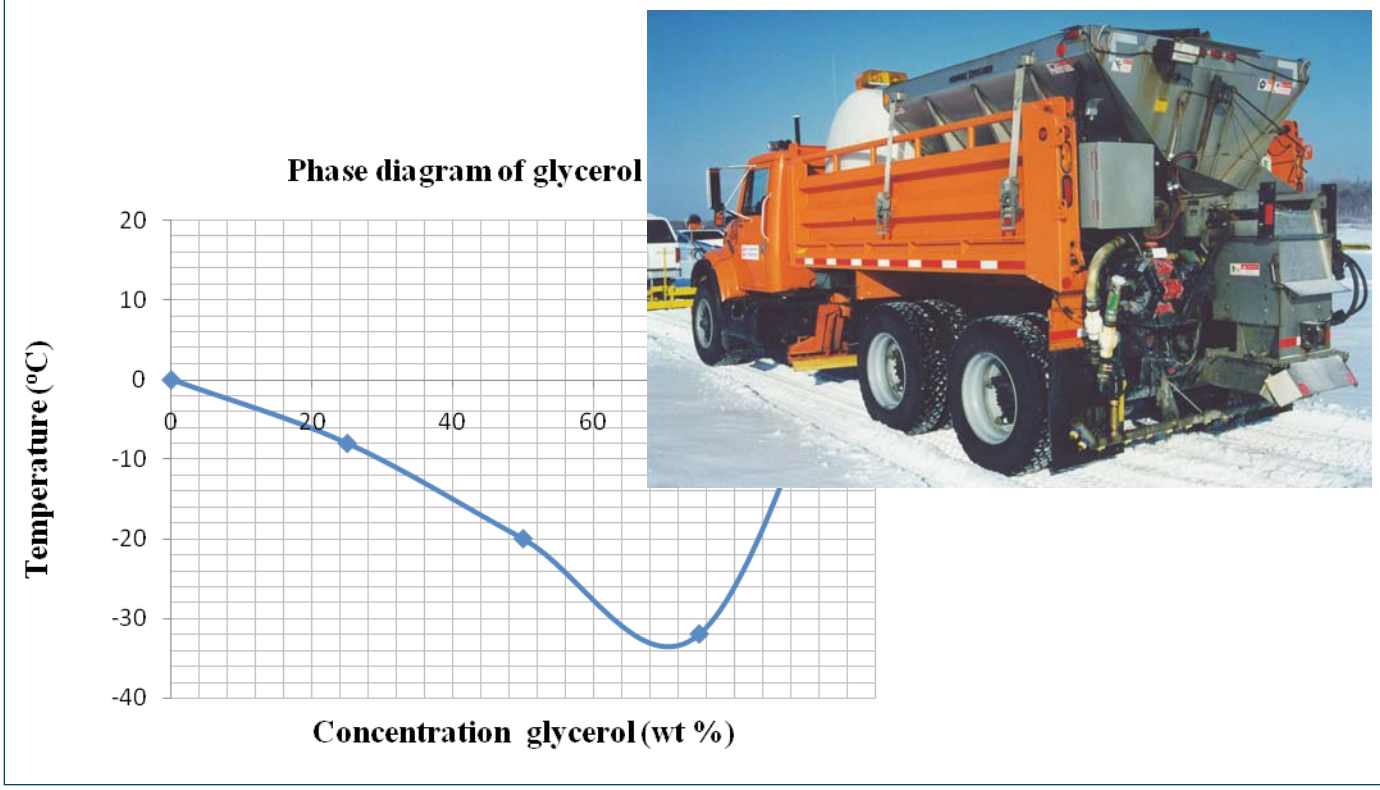

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16. Abstract

Snow and ice removal on public streets is a critical part of the work of departments of transportation in northern U.S. states, including Iowa. Iowa is also a state rich in agricultural resources, some of which undergo industrial processes that generate a number of by-products, e.g., in converting corn to ethanol or soy to biodiesel. It would be desirable to find those that, with a minimum of additional processing, can be used as a deicing compound, either alone or in combination with products currently in use.

The focus of this work is therefore to investigate by-products from agricultural processes that may be suitable for use as deicing applications. This topic has been investigated in the past by others, with many patented products described in the literature. An initial screening was carried out to assess the potential acceptability of selected commercial products, as well as a glycerol developed for this project.

Based on the variety of parameters tested, the product combination that shows the greatest promise for future application consists of 80% glycerol with 20% NaCl.

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DEVELOPMENT OF AN IMPROVED AGRICULTURAL-BASED DEICING PRODUCT

Final Report
January 2010

Principal Investigators
Peter Taylor
Associate Director
National Concrete Pavement Technology Center, Iowa State University

John Verkade
University Professor
Department of Chemistry, Iowa State University

Authors
Peter Taylor, John Verkade, Kasthurirangan Gopalakrishnan, Kuldeep Wadhwa, and Sunghwan Kim

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A report from
Institute for Transportation
Iowa State University
2711 South Loop Drive, Suite 4700
Ames, IA 50010-8664
Phone: 515-294-8103
Fax: 515-294-0467
www.intrans.iastate.edu

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EXECUTIVE SUMMARY

Snow and ice removal on public streets is a critical part of the work of departments of transportation in northern U.S. states, including Iowa. Iowa is also a state rich in agricultural resources, some of which undergo industrial processes that generate a number of by-products, e.g., in converting corn to ethanol or soy to biodiesel. It would be desirable to find those that, with a minimum of additional processing, can be used as a deicing compound, either alone or in combination with products currently in use.

The focus of this work is therefore to investigate by-products from agricultural processes that may be suitable for use as deicing applications. This topic has been investigated in the past by others, with many patented products described in the literature. An initial screening was carried out to assess the potential acceptability of selected commercial products, as well as a glycerol developed for this project.

Based on the variety of parameters tested, the product combination that shows the greatest promise for future application consists of 80% glycerol with 20% NaCl.

INRODUDCTION

Problem Statement

Snow and ice removal on public streets is a critical part of the work of departments of transportation in northern U.S. states, including Iowa.

The issues to be addressed in selecting suitable deicing and anti-icing materials include cost, effectiveness, and damage to the pavement, vehicles, and the environment. The traditional material, sodium chloride, is cheap, but it has a relatively high freezing point and can damage plant life near the pavement. Alternative materials such as magnesium chloride and potassium acetate are reportedly deleterious to the pavement. Organic compounds are reputed to give marginal improvements in performance, but at a relatively high price. Therefore, on balance, there is no ideal material or combination of materials in use at present.

Iowa is also a state rich in agricultural resources, some of which are processed for applications such as fuel. Any industrial process, including that of converting corn to ethanol or soy to bio-diesel, is likely to generate a number of by-products. Rather than face disposal issues for these by-products, it would be desirable to find those that, with a minimum of additional processing, can be used as a deicing compound, either alone or in combination with products currently in use.

Several commercial deicing products have been reviewed by the Iowa Department of Transportation (Iowa DOT), with limited success. Additionally, it is common for these products to be proprietary and therefore often of unknown composition.

The focus of this work is therefore to investigate by-products from agricultural processes that may be suitable for use in deicing applications. An initial screening of selected products was carried out to assess their potential acceptability within the constraints of cost, effectiveness, and side effects.

Research Background

Snow and ice removal is critical for the safe operation of the road transportation infrastructure. Traditionally, sand has been used to provide traction, while cheap salts such as sodium and calcium chloride have been used to melt ice. Both of these approaches have undesirable side effects on the environment, and alternative approaches are continually being sought.

The field of snow and ice removal is well summarized by the *Snowfighters Handbook* (1999) and is the sphere of expertise of consortia such as the Pacific Northwest Snowfighters (PNS) Association. Considerable work has also been published on the relative benefits of different compounds (NCHRP, 2007) and how they can be assessed (Chappelow, 1992).

A negative side effect of deicing pavement surfaces is that the crystallization of salts is expansive and can cause damage to the pavement, particularly if the pavement is concrete. In addition, it has been shown that some of the deicing compounds recently promoted can chemically attack the concrete itself (Sutter, 2007). Use of small entrained air bubbles is the standard means of providing protection from the freezing effects, but work is continuing on finding reliable methods to protect concrete from chemical attack. Materials such as magnesium chloride and potassium acetate are the topics of extensive research and debate as the mechanisms behind their affects are investigated (Rangaraju, 2007; Sutter, 2006, Kozikowski, 2007).

Asphalt surfaces are generally less affected by traditional deicing salts, but compounds containing acetates and formates have been shown to cause distress (Alatyppo, 2007). Ethylene glycol has also been implicated in airfield distress (AAT, 2007).

Organic materials generally have acceptable ice melting performance, but tend to be viscous, potentially leading to problems with placing them uniformly on the pavement, and with reduced skid resistance. This challenge is compounded by the reportedly relatively high costs of these materials on the market. Traditional road salt (NaCl) is reported to cost about $40/ton while calcium magnesium acetate (CMA) costs about $800/ton.

Behind all of these issues is the added concern that the compounds (some including transition (or "heavy" metals) eventually wash off the pavement onto the soil or, in some locations, into water treatment works. Materials that are toxic are therefore not acceptable deicing materials (Lewis, 2001).

Project Objectives

The objective of the work is to seek agricultural-based products that will be suitable for use as deicing materials and that are suitably cost-effective, environmentally acceptable, and technically functional.

LITERATURE SURVEY

A comprehensive literature search was conducted to look for patents or reports of laboratory or field data about agricultural products used as deicing agents, either by themselves or mixed with currently used deicing chemicals. This review also included seeking commercially available products already on the market. Information regarding previous testing conducted on these materials was collected and evaluated.

Deicing Agents

The traditional method of pavement deicing consists of plowing to remove the bulk of the snow cover followed by the application of sand and/or deicing chemicals. Sand improves traction and acts through mechanical action to break down ice. Deicing chemicals act to melt the remaining ice and packed snow and to prevent subsequent snow from accumulating on the pavement surface (Taggart et al., 2002). For example, chloride salts react with snow to form a layer of salty water (i.e., brine) that has a freezing point below 32^{o}F (0ºC). The brine helps to break the bond between the ice and the road surface, which allows the resulting mixture to be plowed from the road (TAC, 1999). A more recent approach has been the application of salts before the snow event, either as solids or as a slurry. These compounds prevent a bond from forming between the pavement and the ice layer, making plowing much simpler and more effective (Pacific Northwest Snowfighters, 2002). A variety of salt compounds are used in this application, including magnesium chloride and potassium acetate.

Sand and sodium chloride (NaCl) have been used as deicing materials in the U.S. since the 1930s (Fischel, 2001). Recent statistics indicate that approximately 10 million tons of NaCl are used per winter in the U.S. (Kuemmel, 1994). NaCl is relatively cheap to purchase; however, its use is not ideal because of the potential for corrosion of reinforcement, corrosive damage to automobile bodies, and pollution due to concentrations of sodium and chloride in roadside soils and water runoff (Zenewitz, 1977; Mehta, 1986; Nadezhdin et al., 1988; Adkins and Christiansen, 1989; Neville, 1996). Alternative materials to NaCl have been researched and employed by many highway agencies. In recent years, there has also been a shortage of this material, leading to increased costs and renewed interest in alternative materials by pavement owners.

Based on previous studies (Yehia and Tuan 1999; Fischel, 2001), the currently used deicing agents can be divided into the following four groups: (1) sanding materials, (2) chloride-based deicers, (3) acetate-based deicers, and (4) other chemicals deicers.

The chloride-based deicers include magnesium chloride (FreezGard Zero® with Shield LS®, Ice-Stop™ CI, Caliber™ M1000, Ice Ban™ M50, etc.), calcium chloride (Liquidow*; Armor*, etc.), and sodium chloride (road salt and Ice Slicer®, etc.). The acetate-based deicers include calcium magnesium acetate (CMA®), potassium acetate (CF7®, etc.), sodium acetate (NAAC®), and CMAK™ (a mixture of CMA and potassium acetate). Other chemical deicers include urea, formamide, and tetrapotassium pyrophosphate (TKPP). Detailed information regarding each of these deicers as well as sand is provided by Yehia and Tuan (1999) and Fischel (2001).

NCHRP 577 report (Levelton 2007) provides detailed guidelines for the selection of snow and ice control materials through an evaluation of their cost, performance, and impacts on the environment and infrastructure. NCHRP 577 report classified the deicing materials into chloride salts, organic products, nitrogen products and abrasives, as shown in Table 1. In this classification, the deicer materials derived from agricultural by-products are included as organic products. Some hybrid deicer material mixtures combining chloride salts and agriculturally derived organic product are also available to reduce corrosion (Levelton Consultants, Ltd., 2007). The general properties of chloride salts and organic products including agricultural by-products reported in NCHRP 577 report are re-presented in Tables 2 and 3.

Table 1. Deicing materials classified in NCHRP 577 report (Levelton Consultants, Ltd., 2007)

Material Type	Snow and Ice Control Material	Primary Components
Chloride Salts	Sodium Chloride (NaCl)	Na, Cl
	Calcium Chloride ($CaCl_2$)	Ca, Cl
	Magnesium Chloride ($MgCl_2$)	Mg, Cl
Organic Products	Calcium Magnesium Acetate (CMA)	Ca, Mg, $C_2H_3O_2$
	Potassium Acetate (KA)	K, $C_2H_3O_2$
	Agricultural By-Products	Complex sugars
	Manufactured Organic Materials	Varies with product (i.e. glycol, methanol)
Nitrogen Products	Urea	Urea, Ammonia
Abrasive	Abrasives	Varies with the source of the material

Table 2. General properties of chloride salts (Levelton Consultants, Ltd., 2007)

Material	Chemical Formula	Forms Used	Optimum Eutectic Temperature °C (°F) @ % Concentration [1]	Common Sources	Approximate Annual usage Tonnes (Tons) North America	Median Cost (USD) per Ton (survey of Internet contracts) [2]
Sodium Chloride	NaCl	Primarily solid, but increasing use of liquid	-21 (-5.8) @ 23.3%	Mined from natural deposits, solarization of natural brines	21,080,000 (22,291,000) (Salt Institute)	$ 36
Calcium Chloride	$CaCl_2$	Mostly liquid brine, some solid flake	-51 (-60) @ 29.8%	Natural well brines, by-product of the Solvay process	Not Available	$120
Magnesium Chloride	$MgCl_2$	Mostly liquid brine, some solid flake	-33 (-28) @ 21.6%	Solarization of natural brines, natural well brines, by-product of metallurgical process	Not Available	$ 95
Blended Chlorides	Varies with product	Solid and liquid	Varies with product	Natural well brines, solarization of natural brines, mined from natural deposits	Not Available	$142

[1] Source: (2)
[2] as of October 2003

Table 3. General properties of organic products (Levelton Consultants, Ltd., 2007)

Material	Chemical Formula	Forms used	Optimum Eutectic Temperature °C (°F) @ % Concentration [1]	Common Source(s)	Approximate Annual usage Tonnes (Tons) North America	Median Cost (USD) per Ton (survey of Internet contracts)[2]
Calcium Magnesium Acetate	CaMgAc	Mostly liquid with some solid	-27.5 (-17.5) @ 32.5%	Reaction of Highly Concentrated Acetic Acid with Dolomite Limestone	Not Available	$1280
Potassium Acetate	KAc	Liquid only	-60 (-76) @ 49%	Reaction of Highly Concentrated Acetic Acid with caustic potash (KOH). This reaction produces potassium acetate and water.	Not Available	Not Available
Agricultural By-Products	NA	Liquid only	Usually blended with chloride-based products	Refined from Agricultural base materials	Not Available	Blends $ 108
Other Organic Materials	Glycols Methanol	Liquid only	Varies with product	Varies	Not Available	Not Available

[1] Source: (2)
[2] As of October 2003

The deicer materials used in Iowa include sodium chloride, calcium chloride, and abrasives. Potassium acetate usage is very limited and magnesium chloride is not used. The reported prices of deicer materials in Iowa are listed in Table 4.

Table 4. Unit costs of deicer materials used in Iowa (in 2009)

Deicer materials	Prices
Sodium chloride	$50 per ton
Calcium chloride	Dry bags - $390 per ton ($7.8 per a 50-lb bag) Liquid - $0.65 per gallon
Abrasives	$ 7 per ton
Potassium acetate	$ 2.85 per gallon

Existing Deicing Agents from Agricultural Products

Considerable research has been carried out in recent years on the topic of developing deicers from agricultural by-products. Most of the developed deicer materials are refined from various agricultural feedstock, including corn, wheat, and rice. Currently, little information is known about the actual manufacturing/refining process because most of the developed materials are all proprietary products (patented or commercial) (Levelton Consultants, Ltd., 2007). Little information is available in the technical literature, but information about products was found in the patent literature.

Table 5 lists the exiting deicing agents from agricultural products reviewed in this study. Some of these materials are products available in the market. A detailed description of these deicer materials is presented in Appendix A.

Table 5. Some existing deicing agents from agricultural products

Product Name	Reference	US Patent No.
Desugared molasses	Bloomer, 2002	6416684
Monoalkyl esters	Chauhan et al., 2006	7048871
Starch	Gambino et al., 1998	5849356
Processed agricultural by-product	Hartley et al., 2007	7208101
Corn wet-milling by-products	Janke et al., 1999a	5965058
Cheese brewing by-products	Janke et al., 1999b	5919394
Beer brewing by-products	Johnson et al., 1999	5922240
Urea	Kerti et al., 2001	6319422
Particulate plant material	Koefod, 2000	6156227
Monohydric and polyhedric alcohols	Lockyer et al., 1998	5772912
Alkalinically reduced sugars	Montgomery et al., 2003	6605232
Succinate salts	Berglund et al., 2001	6287480
Alkali metal acetate	Dietl et al., 2005	6955770
Calcium chloride and urea	Ossian et al., 1997	5683619
Non-chloride based liquid deicer	Seo, 2007	7276179
GEOMELT®	Road Solutions, Inc., 2007	-
Magic Minus Zero™ and Magic Salt™	MagicSalt.info, 2007	-
Icenator Liquid Deicer	eHealth Solutions, 2005	-
Bare Ground Solution	Bare Ground Systems, 2003	-
Caliber M1000	Glacial Technologies	-

Yang and Montgomery (2003) attempted to improve the deicing properties of corn steep water (CSW) by treatment with alkali in the presence of glucose. The properties of treated CSW, including (1) freezing temperature, (2) viscosity, (3) specific gravity, and (4) ice meting ability, were compared with those of deicers presently in use. The authors concluded from this study that the CSW alone is not very efficient as a deicer, but treating with alkali monovalent metal hydroxides (NaOH or KOH) can provide more efficient deicer solutions.

Roosevelt and Fitch (2000) evaluated a commercial agriculturally based deicer material, Ice Ban M50, for its effects on snow removal and ice control operations, the environment, and the highway infrastructure. The operational component included a literature review. The environmental component consisted of a turf grass seed germination test, an acute toxicity test for fathead minnows, and a roadside vegetation stress test in accordance with SHRP H-332 and EPA requirements. The highway infrastructure component consisted of concrete scaling and metal corrosion tests. This study concluded that the costs and operational problems associated with using Ice Ban M50 as a pre-wetting agent for NaCl exceeded those associated with using $MgCl_2$ as a pre-wetting agent.

Current Analytical Methods Used to Measure Properties of Deicing Agents

Many jurisdictions have developed internal specifications and test procedures for traditional deicer materials. However, these have often adapted existing standards. The following specifications or reports are recognized as providing standard test methods developed directly for testing deicer materials (Levelton Consultants, Ltd, 2007):

- *Pacific Northwest Snowfighters Snow and Ice Control Chemical Products Specifications and Test Protocols* (PNS, 2002)
- SHRP H-332, *Handbook of Test Methods for Evaluating Chemical Deicers* (Chappelow and Darwin, 1992)
- American Society for Testing and Materials (ASTM)
- American Association of State Highway and Transportation Officials (AASHTO)

The general areas of deicer material testing in these specifications and reports have primarily focused on the following properties (Levelton Consultants, Ltd, 2007):

- Physical—specific gravity, freezing point, eutectic temperature, gradation, and settling ability
- Chemical and environmental—chemical species and toxicity
- Corrosion—atmospheric, concrete, and concrete reinforcing

Detailed information regarding each of these tests is provided in the NCHRP 577 report (Levelton Consultants, Ltd, 2007). The desirable properties of deicing materials include cost-effectiveness; ease of application to the road or other surfaces; low freezing temperature; prevention of ice formation and reduction of the bonding of snow to the surface of the road; low corrosivity to vehicles and pavement reinforcing; biodegradable properties and a small impact on the environment; an ability to penetrate ice and snow on roads; rapid dissolution after application of the solid mixture; persistence on the surface after application; stable composition in storage; and low or no conductivity on surfaces, such that electrical systems are not shorted out (Yang and Montgomery, 2003).

The Iowa DOT has also developed internal requirements for deicing chemical testing and evaluation, which are included in Appendix B. A multi-step evaluation process includes

(1) Pre-qualification,

(2) Laboratory testing,

(3) Operational testing, and

(4) Evaluation and recommendation.

The manufacturer, distributor, or supplier should provide characteristic information and samples of any deicing chemical, mixture of deicing chemicals, or additives. An independent lab should be asked to test the deicer materials provided. Laboratory tests include chemical composition,

environmental impact, friction test, drying time test, and other proposed performance tests (currently being developed by the University of Iowa). In order to fully assess the efficiency and usability of any deicing chemical or deicing chemical additive, an operational test would be performed by one or more Iowa DOT maintenance garages to determine how the product will perform in a real-world setting in Iowa's environment.

A Transportation Pooled Fund called Clear Roads (Clear Roads, 2009) has also been working on development of standardized test procedures for evaluating the effectiveness of agricultural-based deicer materials.

Impacts of Current Agricultural-Based Deicing Agents on Infrastructure, Vehicles, and Environment

Impacts on Infrastructure and Vehicles

Chloride salts as traditional deicer chemicals are well known to affect concrete structures, either through deterioration of the concrete or corrosion of the reinforcing steel (Kosmatka et al., 2002; Mindess, 2002; Levelton Consultants, Ltd, 2007; Sutter et al., 2008). Deterioration of concrete as a result of exposure to chloride salts occurs as the result of physical and chemical mechanisms (Sutter, 2008). Physical mechanisms associated with the repeated application of deicing chemicals result in scaling or crazing of the slab surface (Van Dam et al. 2002). The primary physical mechanisms considered are not exactly clear, but likely involve a combination of increased saturation, thermal stresses generated when a deicer melts ice, and increased osmotic pressures induced as the deicer imbalances the ionic concentration in the capillary pore solution in the concrete (Mindess et al. 2002; Pigeon and Plateau 1995). Chemical mechanisms of the cement paste can also result in dissolution of calcium hydroxide, coarsening of the concrete pore system, and the formation of deleteriously expansive oxychloride compounds (Sutter, 2008).

Diffusion of chloride ions in chloride salts can lead to corrosion of the reinforcing steel, appearing as rust-colored staining, spalling, cracking, and associated deterioration of the concrete (Levelton Consultants, Ltd, 2007; Sutter et al., 2008). Chloride-induced corrosion is complex and not fully understood. It is assumed that chloride ions destroy the passive layer of oxide that forms on reinforced steel by replacing some of the oxides in the passive film, which further causes an increase in ion solubility and conductivity in the concrete cover (Rosenberg et al., 1989; Raupach, 1996). Chloride ions in chloride salts can also lead to localized or general corrosion for motor vehicles (Levelton Consultants, Ltd, 2007).

Chloride salts may also lead to detrimental effects on asphalt pavement. While their impact on skid resistance is still inconclusive, chloride salts can cause loss of the strength and elasticity of asphalt concrete. Exposure to freeze/thaw cycles and deicers has been found to influence the viscosity of the recovered asphalt binder and the gradation of recovered aggregates (Shi et al. 2009).

While the effects of agricultural-based deicers on deterioration of the concrete and asphalt pavements are not well identified, these deicers tend to result in significantly lower corrosion

rates than chloride-based salts (TRB, 1991; McCrum, 1989). The effectiveness of organic inhibitors is related to the extent to which they reabsorb and cover the metal surface. Absorption of the organic inhibitor depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte (Levelton Consultants, Ltd, 2007). Because of this advantage, agricultural-based deicers have been used in conjunction with chloride-based chemicals as corrosion inhibitors.

Wang et al. (2006) evaluated five deicing chemicals (sodium chloride, calcium chloride with and without a corrosion inhibitor, potassium acetate, and an agricultural product). The properties of the paste and concrete subjected to these deicing chemicals included mass loss, scaling, compressive strength, chemical penetration, and micro-structure under freezing–thawing and wetting–drying exposure conditions. Results indicated that the various deicing chemicals penetrated at different rates into a given paste and concrete, resulting in different degrees of damage. Among the deicing chemicals tested, two calcium chloride solutions caused the most damage, and the agricultural deicing product resulted in the least chemical penetration and scaling damage of paste and concrete.

Shi et al. (2009) surveyed a total of 24 winter maintenance professionals, with one from Finland, one from New Zealand, and the rest from the United States representing agencies in 15 different states, to gain insight into the deicer products currently available and used by road maintenance agencies. In this survey, users were asked to rank the advantages of specific deicers with respect to low cost per lane-mile, low effective temperature, high ice melting capacity, ease of application, and overall safety benefits for winter roads based on field experience or research from the respondent's agency, and to provide any further comments on the topic. The rankings were on a scale of 1 to 5, with 1 being the least advantageous and 5 being the most advantageous. The survey results are reproduced in Table 6, where standard deviation is reported only if three or more people responded to that question. The table also notes the number of people who responded.

Users were also asked to rank the disadvantages of specific deicers with respect to corrosion to metal; impacts on concrete and asphalt pavements; impacts on water quality; impacts on soil, vegetation, wildlife, and human health; and overall effects on structures and the environment based on field experience or research from the respondent's agency. A ranking of 1 to 5 represents the least to greatest impacts, respectively. The survey results are represented in Table 7.

Based on the results of these surveys, Shi et al. (2009) concluded that agricultural deicer products were perceived by users to be the most advantageous, with abrasives being the least. No significant difference was reported between chlorides and acetates/formates.

Table 6. Deicers ranked by advantage, with "1" being the least advantageous and "5" being the most (Shi et al., 2009)

Deicers Listed	Low cost per lane mile		Low effective temperature		High ice melting capacity		Ease of application		Overall safety impacts for winter roads	
	Avg. St.Dev.	n	Avg. St.Dev.	n	Avg. St.Dev.	n	Avg. St.Dev.	n	Avg. St.Dev.	n
Abrasives (sand)	2.9 ± 1.7	7	2.4 ± 1.4	7	1.1 ± 0.8	8	4.0 ± 1.1	9	2.3 ± 1.4	9
Abrasives (volcanic)	3.0	1	1.0	1	1.0	1	4.0	1	4.0	1
Abrasives (non-volcanic)	4.0	1	1.0	1	1.0	1	4.0	1	2.0	1
Abrasives (pre-wet)	1.0	1	2.0	1	3.0	1	5.0	1	4.0	1
Sodium Chloride (solid)	4.2 ± 0.8	14	2.5 ± 1.0	15	3.3 ± 1.1	14	4.3 ± 0.9	16	4.3 ± 0.7	16
Sodium Chloride (liquid brine)	4.5 ± 0.6	4	3.0 ± 0.8	4	3.0 ± 0.8	4	4.3 ± 0.5	4	3.8 ± 0.5	4
Sodium Chloride & Abrasives	3.3 ± 0.6	3	2.3 ± 0.6	3	2.3 ± 0.6	3	3.3 ± 0.6	3	3.3 ± 0.6	3
Magnesium Chloride	2.6 ± 1.2	11	3.7 ± 0.8	11	3.4 ± 1.1	11	3.2 ± 0.7	12	3.8 ± 0.6	12
Magnesium Chloride (liquid)	2.0	1	5.0	1	4.0	1	4.0	1	4.0	1
Calcium Chloride	2.8 ± 1.0	9	4.3 ± 0.5	9	3.8 ± 1.2	9	3.1 ± 0.9	9	3.7 ± 0.5	9
Calcium Chloride (liquid)	3.0	1	5.0	1	5.0	1	4.0	1	4.0	1
Clearlane®	3.5	2	5.0	2	5.0	2	4.7 ± 0.6	3	3.7 ± 1.2	3
IceSlicer®	2.8 ± 1.3	4	4.0 ± 0.0	4	4.3 ± 0.5	4	3.8 ± 1.0	4	4.3 ± 0.5	4
Calcium Magnesium Acetate	1.0	1			5.0	1	4.0	1	5.0	1
Potassium Acetate	1.0 ± 0.0	3	5.0 ± 0.0	3	3.7 ± 1.5	3	3.0 ± 1.6	4	3.8 ± 0.5	4
Sodium Acetate	2.5	2	4.5	2	4.5	2	4.0	2	3.5	2
Potassium Formate	1.0	1	2.0	1	2.0	1	4.0	1	3.0	1
Sodium Acetate/Formate blended with Sodium Magnesium Acetate							3.0	1	3.0	1
Ice B'Gone®	4.0	1	5.0	1	5.0	1	5.0	1	5.0	1
Magic/Caliber®	3.0	1	4.0	1	4.0	1	4.0	1	4.0	1
unspecified	2.0	2	4.5	2	4.5	2	3.0	2	4.0	2
De-ice® (beet sugar)	2.0	2	5.0	1	5.0	1	4.0	1	4.0	1
Corn and Sugar beet	1.0	1	3.0	1	2.0	1	1.0	1	4.0	1
Geomelt®										

Table 7. Deicers ranked by impact, "1" having the least impact and "5" having the greatest impact (Shi et al., 2009)

Deicers Listed	Abbreviation	Corrosion to metals		Impact on concrete and asphalt pavements		Impact on water quality		Impact on soil, vegetation, wildlife and human health		Overall effects the en
		average standard dev.	Percent	average standard dev.	Percent	average standard dev.	Percent	average standard dev.	Percent	average sta de
Abrasives (sand)	sand	1.0 ± 0.0	20	1.2 ± 0.4	23	3.5 ± 1.5	70	2.6 ± 1.3	53	2.6 ± 1.
Abrasives (volcanic)		1.0	20	1.0	20	2.0	40	3.0	60	1.0
Abrasives (non-volcanic)		1.0	20	1.0	20	3.0	60	3.0	60	1.0
Abrasives (pre-wet)		1.0	20	2.0	40	5.0	100	4.0	80	3.0
Sodium Chloride (solid)	NaCl (s)	3.8 ± 1.0	76	3.0 ± 0.7	60	2.5 ± 1.1	49	2.7 ± 0.9	53	3.0 ± 1.
Sodium Chloride (liquid brine	NaCl (l)	2.8 ± 1.5	55	2.7 ± 0.6	53	2.7 ± 1.2	53	3.3 ± 0.6	67	3.3 ± 0.
Sodium Chloride & Abrasives	NaCl & sand	3.3 ± 0.6	67	2.0 ± 1.0	40	3.7 ± 0.6	73	3.0 ± 0.0	60	3.0 ± 0.
Magnesium Chloride	$MgCl_2$	3.3 ± 0.8	66	2.9 ± 1.4	58	2.1 ± 0.7	42	2.2 ± 0.8	44	2.9 ± 0.
Magnesium Chloride (liquid)	$MgCl_2$ (l)	4.0	80	3.0	60	2.0	40	3.0	60	3.0
Calcium Chloride	$CaCl_2$	3.4 ± 0.9	69	2.9 ± 1.2	58	2.8 ± 1.3	55	2.6 ± 1.0	51	2.9 ± 1.
Calcium Chloride (liquid)	$CaCl_2$ (l)	3.0	60							
Calcium Magnesium Acetate	CMA	1.0	20	1.0	20	1.0	20	1.0	20	1.0
Potassium Acetate	K-acetate	1.0	20			2.5	50	3.0	60	3.0
Sodium Acetate	Na-acetate									
Potassium Formate	K-formate	0.0		1.0	20	1.0	20	1.0	20	1.0
Sodium Acetate/Formate blended with Sodium Magnesium Acetate	Na-acetate/formate, NaMg-acetate					3.0	60	2.0	40	3.0
Agricultual Based	Agr-based									
Ice-B-Gone		2.0	40	2.0	40	2.0	40	2.0	40	2.0
Magic/Caliber										
unspecified		2.0	40	2.0	40	3.0	60	3.0	60	2.0
De-ice (beet sugar)		1.0	20	2.0	40	2.0	40	2.0	40	2.0
Corn and Sugar beet		1.0	20	2.0	40	4.0	80			
Geomelt						4.0	80	4.0	80	4.0
Other	Other									
Clear Lane		3.0	60	3.0	60	3.0 ± 1.0	60	2.3 ± 0.6	47	2.7 ± 0.
IceSlicer		3.0 ± 0.0	60	2.7 ± 0.6	53	2.0 ± 1.0	40	2.3 ± 1.5	47	3.0 ± 2.
Interstate melt 500		3.0	60	2.0	40	2.0	40	2.0	40	3.0

Impacts on the Environment

All currently available deicer materials can affect the natural environment. NCHRP report 577 (Levelton Consultants, Ltd, 2007) presents a simplified conceptual diagram showing primary transport mechanisms and pathways of deicer materials, as well as areas of effect of deicer materials (See Figure 1). The primary component of currently available agricultural deicer materials is organic matter such as complex sugars, and the secondary attributes of these materials include heavy metals, phosphorus (P), nitrogen (N), and organic matter quantified by biochemical oxygen demand (BOD) (Levelton Consultants, Ltd, 2007).

The organic matter and nutrients of agricultural deicer materials can cause oxygen depletion or eutrophication in water streams, which is critical to aquatic biology. Relatively small amounts of phosphorus can also change aquatic ecosystems drastically. There is limited information detailing the effects of agricultural deicer products on soil properties, but, based on organic constitution, NCHRP report 577 (Levelton Consultants, Ltd, 2007) suggested that they would be subject to degradation by soil micro-organisms. Degradation could lead to anaerobic conditions in the soil, which can decrease soil pH and increase the solubility of adsorbed metals. However, Klecka et al. (1993) reported that high levels of the deicing materials containing glycol are unlikely to be inhibitory to soil microorganisms. The biodegradation rates were very similar regardless of the type of glycol in deicer materials.

Few literature references reported the effects of agricultural deicer materials on vegetation, animal, and human health. This might be a result of the number and variability of available proprietary products. Many of these products are biodegradable, and it is generally assumed that they pose minimal concern for vegetation and animal and human health when compared to other types of deicers products (Levelton Consultants, Ltd, 2007). Small concentrations of phosphorus and ammonia in organic deicer materials can provide nutrients for plant growth. The summary of the effects of deicer materials on the environment is presented by Shi et al. (2009) and reproduced in Table 8.

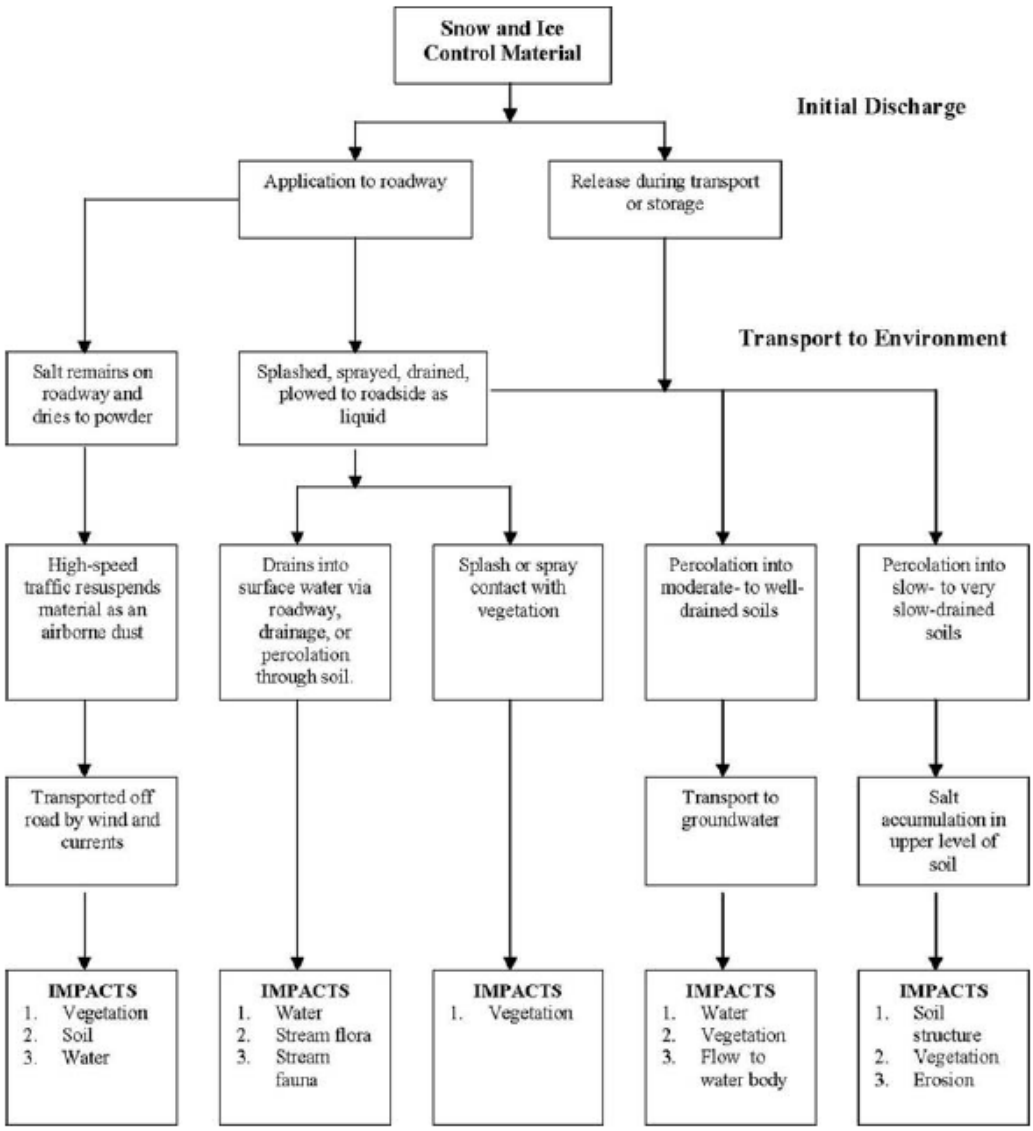

Figure 1. Environmental pathway model of deicer materials (TRB, 1991; Levelton Consultants, Ltd, 2007)

Table 8. Effect of deicer materials on environment (Shi et al., 2009)

	Abrasives	Chloride	Acetate & Formate	Glycol	Urea & Bio/Agr-based
Soil	Will accumulate.	Chloride, calcium, and potassium can mobilize heavy metals. Sodium can accumulate in soil and reduce soil permeability leading to increased soil density. Calcium can increase soil premeability and aeration. Magnesium can increase soil stability and permeability. NaCl can decrease soil fertility, leading to reduced plant growth and increase erosion.	Calcium and magnesium can mobilize heavy metals, increase soil stability, and permeability. CMA degredation may increase soil pH.	Readily biodegrades. Propylene glycol degredation may reduce hydraulic conductivity in anerobic soils.	Use of urea can lead to increased nitrate concentrations. Little data is available on bio/agr-based deicers.
Flora	Can accumulate on foliage and in adjacent soils that contact the roots, potentially causing stress.	Chloride contact with foliage can cause leaf singe, browning, and senesnce. Chloride contact can lead to osmotic stress. Salt tolerant species are recommended for us as roadside vegetation where chloride based deicers are used.	Few effects have been observed. At low concentrations acts as a fertilizer, at elevated concentration reduces seed germination, causing low biomass yield, leaf browning, and senescence.	Glycol can inhibit plant growth.	Little data is available on bio/agr-based deicers.
Surface & Ground Water	Can increase turbidity, decrease gravel, and rock poor space leading to limited oxygen supply.	Chloride, sodium, calcium, and potassium ions easly go into solution, migrate, and can harden the water. Can cause density stratification in small receiving waters potentially causing anoxic conditions at depth. Potassium and calcium can mobilize heavy metals in water. Potassium can cause eutrophication of water.	Can leach heavy metals from soil that can trasport into water. Has a high BOD and can cause oxygen depletion. Can increase turbidy and hardness of water.	Can increase BOD to a greater extent than any other deicer. Degrades in water faster than additives which can be toxic. Readily biodegrades.	Use of urea can lead to increased nitrate concentrations. Urea additives can be toxic. Little data is available on bio/agr-based deicers.
Fauna	Can reduce oxygen in strem beds and cause increased turbidity.	Chlorides have little to no impact when ingested unless extremely elevated concentrations are reached. Direct ingestion of salts by mammals and birds has caused behavior changes and toxicity. Concentrations of 250 mg/L have been shown to cause changes in community structures. Use of chlorides on roadways may lead to increased wildlife-vehicle collisions.	Can exert a high BOD which may cause anoxic conditions in aquatic environments. KAc and NaAc appear to be more toxic than CMA. Can promote bacteria and algae growth.	Ingestion of concentrated fluid can lead to death. A known endocrine disrupter.	Little data is available on bio/agr-based deicers.
Human	Can cause increased PM10 and can lead to air quaility non-attianment issues. Can reduce stream visibility, alter stream and roadside habitat, and decrease asthetics.	Skin and eye irritant. Drinking water with sodium concentrations >20 mg/L can lead to hypertension. Can increase chloride, calcium, potassium, and sodium concentrations above recommendations. Anti-caking agents may contain cyanide a known carcinogen.	Skin and eye irritant. Calcium and magnesium can increase water hardness.	Ingestion of concentrated fluid can lead to death. A known endocrine disrupter.	Use of urea can increase nitrate levels in water. Little data is available on bio/agr-based deicers.

SELECTION OF DEICER MATERIALS FOR EXPERIMENTAL TESTING

Based on the information collected in the literature review and discussions with faculty at Iowa State University (ISU) involved with research into other uses for agricultural by-products, several compounds or mixtures were selected for the development of alternative deicers based on agricultural products. The selection of these materials was made in consultation with this project's Technical Advisory Committee (TAC). Selections were based on the following considerations:

- Likely efficiency as a deicing or anti-icing compound
- Usability
- Likely effects on skid resistance
- Likely cost and availability
- Likely damage to the pavement
- Likely damage to vehicles
- Likely effects on the environment

Chloride-based deicers (NaCl and $MgCl_2$), considered to be traditional deicers, were used as control materials against which the performance of the others could be compared.

The commercial agricultural-based deicers selected for testing in this study were Geomelt® and Ice B Gone®. Geomelt® is derived from a renewable sugar beet source (Road Solutions, Inc, 2007) and Ice B Gone is manufactured from a molasses, high-fructose corn syrup, or other carbohydrate base (Sears Ecological Applications Company, 2009). Combining one of these materials with salt (NaCl) can allow for lower salt application rates on roads with equal or superior performance to that of only traditional deicer.

Two types of commercial agricultural by-products from biofuel production were also selected for laboratory testing. The commercial brand names of these materials are BioOil and E310, which have not been used and studied before as deicers. The BioOil was obtained from a commercial biomass conversion facility located in Canada. The BioOil is a dark brown, free-flowing liquid fuel with a smoky odor reminiscent of the plant from which it is derived. It is formed in a process called fast pyrolysis, wherein plant material (biomass), such as forest residues (bark, sawdust, shavings, etc.) and agricultural residues (sugar cane, cornhusks, bagasse, wheat straw, etc.), are exposed to 400–500°C in an oxygen-free environment (Dynamotive Energy Systems Corporation, 2007). BioOil has been used as a boiler fuel. The E310 was obtained from a full-scale, wet-mill, corn-based ethanol plant of Grain Processing Corporation (GPC) in Muscatine, Iowa (Grain Processing Corporation, 2009). Alkaline-washed corn hull is obtained in the process of converting the corn into ethanol, and co-product B is a powdered version of this. The E310 has been used in animal feed applications.

Another type of agriculturally derived organic product is glycerol (aka glycerine, glycerin). It is a colorless, odorless, and viscous liquid, and its very low toxicity allows its wide use in pharmaceutical, personal care, and food formulations. Glycerol, $HOCH_2CH(OH)CH_2(OH)$, has three hydrophilic hydroxyl groups that are responsible for its solubility in water and

its hygroscopic nature. The glycerol substructure, $OCH_2CH(O)CH_2(O)$, is a central component of many fats and lipids. For example, it links together the three fatty acid portions of triglycerides that bind to the oxygens by replacing the hydrogens.

Glycerol is easily obtained as a by-product during the saponification of animal fats by treatment with sodium or potassium hydroxide in soap manufacture. Glycerol is also an easily obtained by-product in the production of biodiesel via treatment of animal fats and a wide variety of plant oils with methanol in the presence of catalytic amounts of sodium methylate or basic organic compounds in a process known as transesterification (Venkat et al., 2007).

Because of the vigorous activity in the development of the biodiesel market, the market for glycerol is depressed. Approximately 950,000 tons of biodiesel per year are currently produced in the U.S. and Europe, which translates to the co-production of about 99,000 tons of glycerin per year. Biodiesel manufacture will increase as European Union directive 2003/30/EC is implemented. This directive requires the replacement of 5.75% of petroleum fuels with biofuel in all member states by 2010 (Biodiesel, 2009).

Like ethylene glycol and propylene glycol, glycerol is very soluble in water. Its minimum freezing point is at about -36 °F (-37.8 °C), which is reached by a solution of 60%–70% glycerol in water.

Samples of the selected materials were obtained from appropriate sources, either commercial facilities, laboratories, or processing facilities at ISU.

LABORATORY TESTS AND RESULTS

Laboratory tests were conducted on the selected materials that can either be combined with existing deicing chemicals (NaCl or $MgCl_2$) or used alone. These tests were designed to investigate whether the agricultural-based deicers have the potential to meet the requirements of maximum effectiveness and minimum side effects. Based on the guidance provided in the SHRP H-332 report (Chappelow and Darwin, 1992), *Handbook of Test Methods for Evaluating Chemical Deicers*, the tests included determination of the following:

- Freezing points with eutectic temperature (SHRP H-332, Clause 3.1.5)
- Ice melting ability (SHRP H-205.1 and 2)
- Skid resistance (ASTM E 303)
- Viscosity

Freezing point, ice melting ability, and viscosity tests were conducted at the Chemistry Department Laboratory at ISU. Skid resistance tests were carried out at the Portland Cement Concrete (PCC) Laboratory at ISU.

The combinations selected for testing were as shown in Table 9.

Table 9. Materials combinations selected for laboratory testing

I.D.	Combination
A	100% glycerol
B	90% glycerol + 10% $MgCl_2$
C	80% glycerol + 20% NaCl
D	90% Geomelt® + 10% $MgCl_2$
E	80% Geomelt® + 20% NaCl
F	90% Ice B Gone® + 10% $MgCl_2$
G	80% Ice B Gone® + 20% NaCl
H	5% solution of NaCl in water
I	50 % E310 + 50% glycerol
J	100% NaCl
K	40% E310 + 40% glycerol + 20% NaCl
L	50% glycerol + 50% $MgCl_2$

Freezing Points and Ice Melting Tests

Freezing Points Test with Eutectic Temperature

The freezing points of water solutions of the selected combinations were determined. Solutions of each combination were cooled slowly with stirring, while time and temperature were recorded. Each combination was evaluated over a range of concentrations in water: 25%, 50%, 75%, and 100% by solution weight. The freezing temperature was determined as the temperature

at which the first ice crystals form. The phase diagram of each combination was constructed to determine eutectic temperature and concentration using the recorded freezing temperatures. All the phase diagrams developed are presented in Appendix C. Figure 2 shows the phase diagram for combination A (100% glycerol) for illustration purposes. Eutectic temperature was determined as the lowest temperature in the phase diagram for a given combination. Eutectic concentration is the concentration corresponding to the eutectic temperature. As seen in Figure 2, the eutectic temperature of combination A (100% glycerol) is -34^{o}C, and the eutectic concentration is 70%.

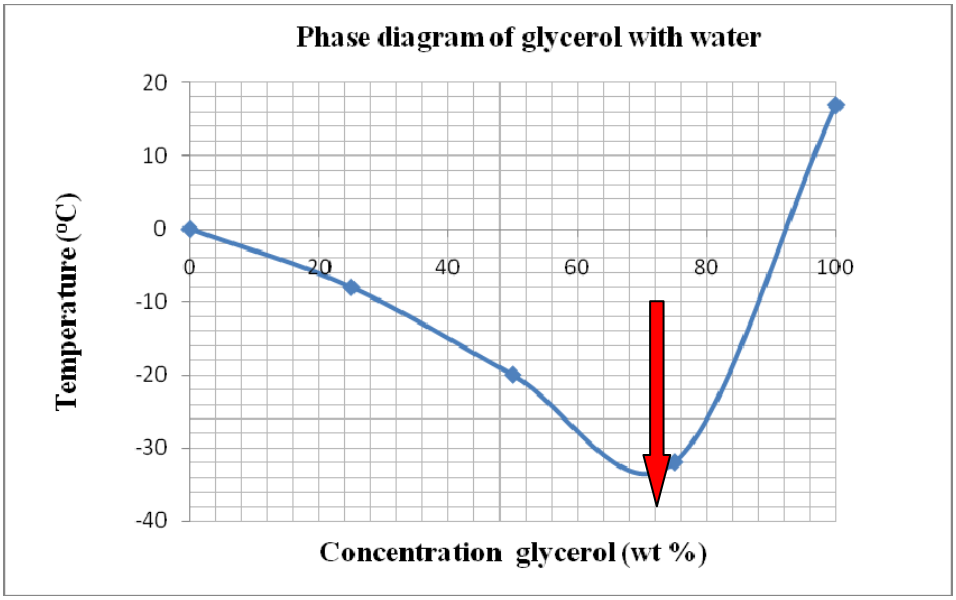

Figure 2. Phase diagram of combination A (100% glycerol) in water

Ice Melting Test

This test provides information on the time-dependent quantities of ice melted by a deicer, which can be used to evaluate new or modified deicers in comparison to existing deicers (Chappelow and Darwin, 1992). This test has been considered a primary method for evaluating chemical deicers (Chappelow and Darwin, 1992). In this test, 25 mL water was placed in a flat-bottom dish and frozen in a constant temperature bath at -12^{o}C to form a 1/8 inch solid layer. To this was added 25% of each combination group by solution weight. The volume of water that melted was recorded at regular intervals of time. Figure 3 presents the rate of ice melting of combination A (100% glycerol) in water for the purposes of illustration. The results of the rate of ice melting tests for all combinations are presented in Appendix C.

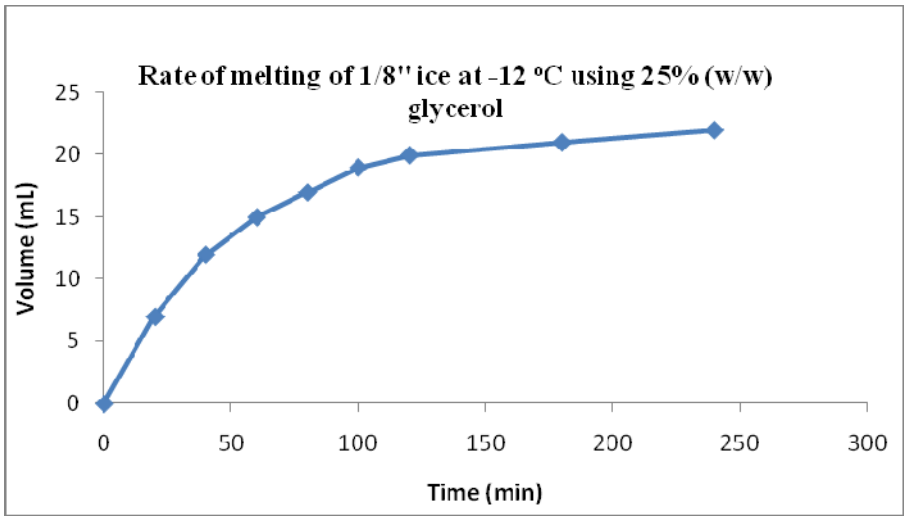

Figure 3. Rate of ice meting for 25% of combination A (100% glycerol) in water

Skid Resistance Test

A portable skid resistance tester, British pendulum tester (BPT), was used to measure skid resistance on a concrete surface coated with various deicer combinations in accordance with ASTM E 303. Figure 4 displays the portable skid resistance tester used in this study next to a coated surface. In this test, the pendulum of BPT is released from the horizontal position, and the rubber slider at the bottom of the pendulum contacts the coated surface for a fixed previously set length. The greater the friction between the slider and the coated surface, the more the swing is retarded. A drag pointer that moves with the pendulum during the forward part of its swing indicates a scale reading defined as British pendulum number (BPN). Higher BPN indicates greater skid resistance. The European standard EN 1436 specifies that BPN should be higher than 45 (Wallman and Astrom, 2001).

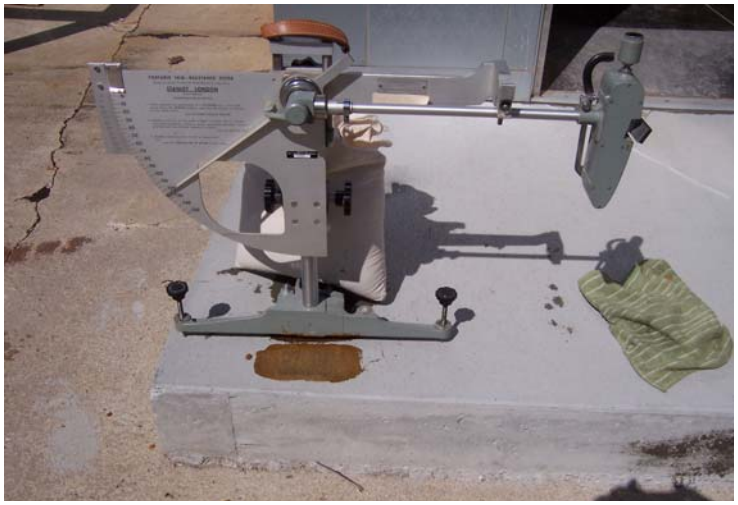

Figure 4. Portable skid resistance tester near coated surface

Table 10. Results of skid resistance test

ID	Description	Average BPN
A	100% glycerol	37.7
B	90% glycerol + 10% $MgCl_2$	36.7
C	80% glycerol + 20% NaCl	52.3
D	90% Geomelt® + 10% $MgCl_2$	51.0
E	80% Geomelt® + 20% NaCl	39.0
F	90% Ice B Gone® + 10% $MgCl_2$	42.7
G	80% Ice B Gone® + 20% NaCl	43.0
H	5% solution of NaCl in water	65.0
M	50% Glycerol + 50% Ice B Gone	34.3
N	90% BioOil + 10% $MgCl_2$	45.0
O	80% BioOil + 20% NaCl	38.0
P	Wet	66.0
Q	Dry	85.3

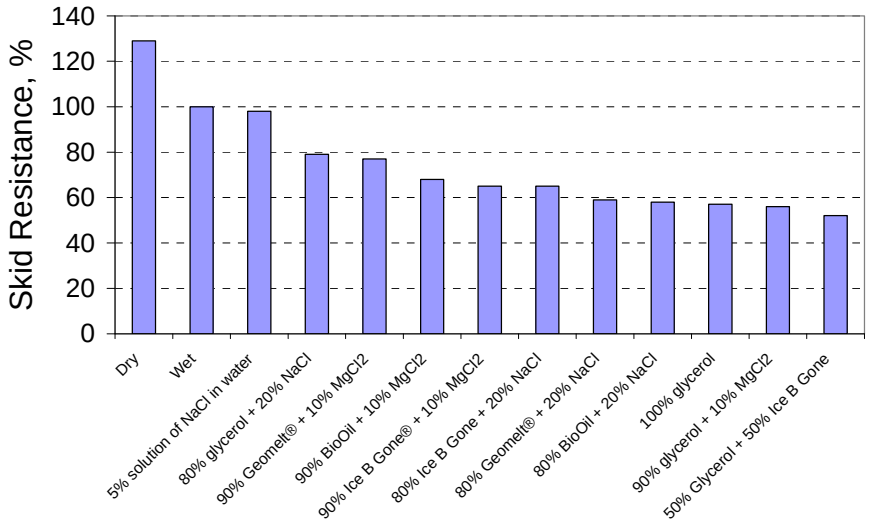

Figure 5. Skid resistance results for various deicer combinations

Discussion

Table 11 summarizes the results of the experimental tests conducted on the various deicer combinations. The freezing temperatures and ice melting volumes reported in this table are measurements corresponding to a 75% concentration of each combination in water and 240 minutes, respectively. The skid resistance percentage reported is the percentage of the BPN on each combination-coated surface relative to the BPN on the surface treated with plain water (100%).

Table 11. Summary of experimental test results

I.D	Description	Freezing temperature, °F	Eutectic temperature, °F	Ice melting, ml	Skid resistance,%
A	100% glycerol	-32	-34	22	57
B	90% glycerol + 10% $MgCl_2$	-44	-45	24	56
C	80% glycerol + 20% NaCl	-46	-48	25	79
D	90% Geomelt® + 10% $MgCl_2$	-23	-*	9	77
E	80% Geomelt® + 20% NaCl	-37	-	11	59
F	90% Ice B Gone® + 10% $MgCl_2$	-48	-	25	65
G	80% Ice B Gone® + 20% NaCl	-50	-	25	65
H	5% solution of NaCl in water	-3	-	17	98
I	50 % E310 + 50% glycerol	-14	-15	13	-
J	100% NaCl	-	-	25	-
K	40% E310 + 40% glycerol + 20% NaCl	-41	-42	20	-
L	50% glycerol + 50% $MgCl_2$	-	-	25	-
M	50% Glycerol + 50% Ice B Gone	-	-	-	52
N	90% BioOil + 10% $MgCl_2$	-	-	-	68
O	80% BioOil + 20% NaCl	-	-	-	58
P	Wet	-	-	-	100
Q	Dry	-	-	-	129

* Could not be tested due to difficulties associated with preparing the combination for testing

The approach to assessing the overall performance of the different combinations was to highlight the best performing combinations for each test parameter.

Based on the variety of parameters tested, the combination that shows the greatest promise is a combination of 80% glycerol with 20% NaCl.

When considering other parameters, such as corrosive effects to steel, the dilution of NaCl will help reduce these effects while the addition of glycerol will not increase the risk. Likewise, the effects of glycerol on plant life are reported to be minimal.

The greatest concern about the use of this combination will be in handling the product and applying it to the pavement due to its viscosity.

For this reason, the viscosity of the combination of 80% glycerol with 20% NaCl was measured at different concentrations in water. The results, presented in Figure 6, indicate that the viscosity of this combination can be controlled by its concentration in water. In terms of practical application in the field, it seems feasible to use this combination with the Iowa DOT deicer spray truck at a reasonable concentration-to-flow ratio.

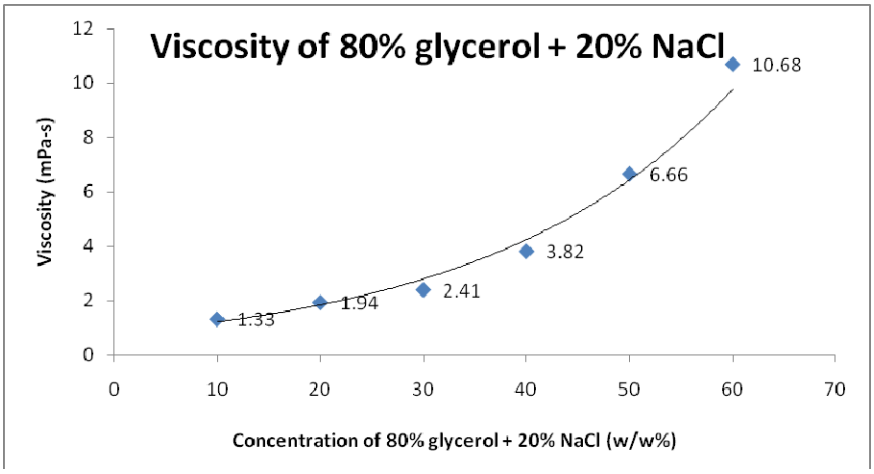

Figure 6. Viscosity of 80% glycerol with the 20% NaCl combination at different concentrations in water

CONCLUSIONS

Based on a review of the literature and an experimental program, it is concluded that a mixture of 20% NaCl with 80% glycerol diluted to a viscosity suitable for distribution equipment shows promise as a deicing chemical based on agricultural by-products.

The next stage of work necessary will be to investigate what resources are required to produce the product in large quantities. A pilot demonstration of production and use in Iowa DOT equipment during a winter storm is recommended.

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APPENDIX A. SURVEY RESULTS FOR DEICING AGENTS FROM AGRICULTURAL PRODUCTS BASED ON LITERATURE REVIEW

A comprehensive literature search was conducted looking for patents or reports of laboratory or field data about agricultural products used as deicing agents, either by themselves or mixed with existing deicing chemicals. This review also included seeking commercially available products already on the market. Information regarding previous testing conducted on these materials was collected and evaluated. Most of the information (text, tables, and figures) reported in this section is drawn from the references cited as is.

Deicing Agents

The typical method for pavement deicing consists of plowing to remove the bulk of the snow cover followed by the application of sand and/or deicing chemicals. Sand improves traction and acts through mechanical action to break down ice. Deicing chemicals act to melt the remaining ice and packed snow and to prevent subsequent snow from accumulating on the pavement surface (Taggart et al. 2002).

Sand and sodium chloride (NaCl) have been used for deicing material in the U.S. since the 1930s (Fischel 2001). The recent statistics indicate that approximately 10 million tons of NaCl are used per winter in the U.S. (Kuemmel 1994). However, the use of NaCl causes many problems, which include damage to concrete pavement and bridge decks (e.g., surface scaling and corrosion of reinforcement), corrosive damage to automobile bodies, and pollution due to concentrations of sodium and chloride in roadside soils and water runoff (Zenewitz 1977; Mehta 1986; Nadezhdin et al. 1988; Adkins and Christiansen 1989; Neville 1996). Alternative materials to use of NaCl have been searched and used by many highway agencies.

Based on previous studies (Yehia and Tuan 1999; Fischel 2001), the currently used deicing agents can be divided into the following four groups: (1) sanding materials, (2) chloride-based deicers, (3) acetate – based deicers, and (4) other chemicals deicers. The chloride-based deicers include magnesium chloride (FreezGard Zero® with Shield LS®, Ice-Stop™ CI, Caliber™ M1000, Ice Ban™ M50), calcium chloride (Liquidow*; Armor*), and sodium chloride (road salt and Ice Slicer®). The acetate-based deicers include Calcium Magnesium Acetate (CMA®), Potassium Acetate (CF7®), Sodium Acetate (NAAC®), and CMAK™ (a mixture of CMA and Potassium Acetate). The other chemical deicers include urea, formamide, and tetrapotassium pyrophosphate (TKPP).
Detailed information regarding each of these deicers as well as sand is provided by Yehia and Tuan (1999) and Fischel (2001).

Reported Deicing Agents from Agricultural Products

Desugared molasses (Bloomer, 2002)

The composition is formed from a waste product of the process of removing sugar from molasses, also known as desugared molasses. As a byproduct of a widely used process for making edible sugar, the desugared molasses is readily available at a low cost. Moreover, the composition is

ready for use in conventional spraying equipment without the need for mixing agents, is environmentally friendly, and is able to perform at temperatures well below the freezing point of water. The composition is also non-corrosive and can be admixed with chloride salts, such as magnesium, calcium, or sodium chloride, to reduce the corrosiveness of the resulting solution while still providing effective deicing activity. Bloomer (2002) applied the pure desugared molasses and the pure desugared mixed with chloride salts on concrete pavement. The result shows all of these materials melted snow and ice very well.

The typical composition of the desugared molasses reported is presented in Table 1.1.

Table 1.1: Typical Composition of Desugared Molasses

Item	Content *
Moisture	40%
Fructose Polymers	15%
Amino Acid Polymers	12%
Other Carbohydrates, Starches and Polymers	17%
Potassium	9%
Sodium	3%
Chloride	1%
Other Ash/Calcium Oxide	3%

**All measurements are approximate.*

Other physical characteristics of desugared molasses are listed below in Table 1.2.

Table 1.2: Selected Physical Characteristics of Desugared Molasses

Characteristic	Quantity
Weight	10.7 pounds/gallon
PH	9 – 10
Freezing Point	<-30°F
Boiling Point	212°F
Viscosity	150 cp at -30°F
Color	dark brown
Odor	chocolate

Monoalkyl esters (Chauhan et al., 2006)

A deicing/anti-icing fluid can be produced from a byproduct stream obtained from a process that produces alkyl esters, preferably monoalkyl esters of long chain fatty acids. The stream includes at least water, glycerol, and an alkali-containing compound. The byproduct stream can be obtained from any suitable alkyl ester process. Some non-limiting examples of processes that can produce suitable byproduct streams include animal fat rendering, vegetable oil hydrolysis, and

soap making. The byproduct stream is converted to a deicing/anti-icing fluid by adding an acid to the stream to neutralize the alkali-containing compound to produce an alkali salt that functions as a supplemental freezing point depressant. The alkali salt works in combination with the glycerol, which is the primary freezing point depressant.

The process makes beneficial use of byproducts that would otherwise require further processing or disposal. Specifically, the process makes use of the glycerol in the byproduct stream as the primary freezing point depressant. Advantageously, the glycerol is nontoxic to the environment. The process also makes use of the alkali-containing compound in the byproduct stream that was considered to be a contaminant, by converting the material to a supplemental freezing point depressant. Thus, the invention eliminates the expense of removing the contaminant from the byproduct stream. In view of these advantages, the process achieves the low cost production of a deicing/anti-icing fluid.

Some typical and preferred ranges of ingredients of the deicing/anti-icing fluids are shown in Table 1.3.

Table 1.3: Composition of Alkyl Ester Fluid Solution Utilized for Roadway/Runway Deicing

Component	Typical Range		Roadway/Runway Deicing Preferred Range	
	Low %	High %	Low %	High %
Glycerol	15	88	20	85
Alkali Salt	1	20	5	20
Additional Freezing Point Depressant	0	40	5	40
Buffer	0	2	0.05	0.5
Corrosion Inhibitor	0	2	0	0.1
Preservative	0	0.1	0.001	0.01
Water	10	70	12	50

For application of deicing/anti-icing fluid on roadways, it is not necessary to provide freeze protection down to -60°C. Also, the glycerol provides corrosion protection against salt corrosion. Finally, the fluid can be used as a brine or as a pre-wetting agent for road salt, which reduces corrosion potential that salt alone.

Starch (Gambino et al., 1998)

It has been discovered that a small amount of starch added to the salt/water deicing solution sprayed on highways provides the property of retaining salt particles in the top portion of the "voids" in asphalt roads for a period of 2 to 4 hours. The starch can be incorporated into water by mixing; biocides can be added if the starch/water mixture is to be stored more than 2 days. Salt is added to the water/starch mixture prior to deposition on the road. The new treatment works by increasing the viscosity of the aqueous fluid sprayed on the highway to form a water gel structure on the road providing a "platform" for the salt particles in the top portion of the asphalt.

The typical composition of the deicing solution is shown in Table 1.4.

Table 1.4: Typical Composition of Starch/Water/Salt Deicing Mixture

Component	Typical Range*	
	Low %	High %
Water (@ ≤ 65°C)	10	97
Starch	0.5	30
Salt	5	90

** All percentages are calculated by volume and are relative to the other components.*

The starch selected for the deicing solution can be selected from both natural starch and starch derivatives. Wheat-based starches and derivatives have been found particularly effective for use in the present invention. These starches have the additional advantage of being especially biodegradable, and to be particularly resistant to salt degradation. Preferred forms of salt for use in this invention are the various grades of sodium chloride, rock salt, and calcium chloride salt currently used for highway maintenance and deicing in the United States.

The most efficient use of the starch additive treatment is as a pre-treatment process and product. The starch additive also reduces the need and cost of "follow-up" salt treatments. Additionally, the starch/water/salt mixture may be frozen and thawed repeatedly without change in physical properties, which is particularly desirable for road maintenance departments.

Gambino et al. sprayed an asphalt block with a starch solution. The asphalt block was then stored in a freezer at -10°C, -15°C, and -20°C. No ice formation was observed on the treated asphalt block at both -10°C and -15°C. The treated asphalt block showed a few traces of ice at -20°C at spots with inadequate distribution of the solution.

Processed agricultural by-product (Hartley et al., 2007)

The basic composition of the deicing formulation consists of at least the first two of the following three components in aqueous solution:

(1) Inorganic freezing point depressants preferably in the form of chloride salts, which include magnesium chloride, calcium chloride and sodium chloride. Metal acetates e.g., calcium magnesium acetate, may also be used.
(2) At least one agricultural product selected from brewer's condensed solubles (BCS), distillers condensed solubles (DCS) and/or condensed corn steep liquor (CCSL) which contains a low molecular weight carbohydrate fraction in the 180 to 1,500 range (180 1,000 preferred).
(3) Thickeners are optionally used in certain applications as the third component to increase the viscosity of the composition so that the liquid remains in contact with the road surface or with the solid particles in piles of salt, sand, aggregate, or mixtures thereof.

These components are used in an aqueous solution in the concentrations presented in Table 1.5.

Table 1.5: Typical Composition of BCS/DCS/CCSL Deicing Solution

Component	Weight %
BCS/DCS/CCSL*	3 to 60
Inorganic Freezing Point Depressant	5 to 35
Thickener	0.15 to 10
Water	Balance

***** *Wt % of low molecular weight carbohydrate fraction included in BCS, DCS and steepwater*

It has been determined that the presence and concentration of low molecular weight carbohydrates has a synergistic effect on the freezing point and ice/snow melting characteristics of chloride containing liquid deicers. Therefore, for each of BCS, DCS and CCSL, there is a minimum low molecular weight carbohydrate fraction concentration that is necessary for suitable performance as a deicing formulation component. This necessary minimum concentration in weight % is different for each of these carbohydrates and is tabulated in Table 1.6 below.

Table 1.6: Minimum Low Molecular Weight Carbohydrate Fraction Concentration

Agricultural Product	Weight %
BCS	25.0
DCS	8.0
CCSL	6.0

The formulation has a viscosity of 100 to 140 centipoises at 0°C (32°F). Also, the suspended solids and crude fiber create difficulties during storage and blockage of spray tips during application of liquid deicers/anti-icers made with BCS. However, commercially large amounts of a BCS/$MgCl_2$ aqueous solution were used throughout one winter season with excellent results, and the storage characteristics were also quite satisfactory.

Corn wet-milling by-products (Janke et al., 1999)

The steepwater deicing composition is a by-product of a milling process of grain, such as the wet milling of shelled corn, wheat, sorghum, barley or soybeans. The deicing composition can be applied to road surfaces prior to the accumulation of snow and ice, which application will help prevent the snow and ice from adhering to the road surfaces. Subsequent to the accumulation of snow and ice, the steepwater composition is again applied, but this time to reduce the accumulated freezing precipitation such as snow and ice. The two-step application facilitates removal of the accumulated snow and ice by plows and other mechanical methods. The deicing composition also acts as a corrosion inhibitor and fertilizer.

Steepwater deicing compositions may comprise by weight less than 100% steepwater solubles as shown in Table 1.7.

Table 1.7: Composition of Steepwater Deicer Fluid

Component	Typical Range		Preferred Range	
	Low %	High%	Low %	High %
Steepwater	3	95	14	80
Water	5	97	20	86

Compositions may be further admixed with optional additives such as skid-reducing agents and conventional deicing and anti-freeze compositions. The percentage by weight of steepwater solubles and the percentage by weight of any accompanying liquid vary with the needs of the user. When the steepwater solution is admixed with skid reducing agents, the skid reducing agents may compromise greater than 50% by weight of the admixture.

A 50% steepwater soluble-50% water composition has a freezing point below 0°F. It is liquid and free flowing at +10°F and can be easily sprayed and applied to road surfaces or accumulated ice or snow at ambient temperatures. The composition can also be heated before its application to allow spray application at lower temperatures. The composition may be preferably applied onto the road surface from moving vehicles in an amount of about 20 to 60 gallons per lane mile, which is about 200 to about 600 pounds per lane mile.

Steepwater deicing compositions are water soluble, negligibly corrosive, inexpensive and widely-available in large quantities. Steepwater solubles are also safe and possess no undue hazards to humans, animals or the environment from the handling, storing, or use of steepwater even when concentrated. The composition is a renewable agricultural by-product, and its commercial usage will help support U.S. farmers and the agricultural industry.

Cheese brewing by-products (Janke et al.,1999)

A deicing composition can be produced from by-products from the production of cheese from various milks. More specifically, the composition is comprised of the liquids that remain after the coagulated cheese has been removed from the milks, which is commonly known as "whey." Typically, whey is evaporated to the point that the liquid contains about 50% solubles, and then the evaporated whey is used as an animal feed additive.

Though the actual composition of whey varies, the representative composition of whey reported is presented in Table 1.8.

Table 1.8: Representative Composition of Whey

Item	Dry Basis (no moisture)	Condensed (50% solids/50% moisture)
Protein	12.80%	6.20%
Crude Fat	0.20%	0.10%
Carbohydrates	74.13%	37.07%
Calcium	4.20%	2.10%
Iron	1.10%	0.55%
Magnesium	1.30%	0.65%
Phosphorous	2.11%	1.06%
Potassium	4.64%	2.32%
Sodium	0.58%	0.29%
Zinc	0.20%	0.10%
Amino Acids	1.01%	0.51%
Lipids	0.24%	0.12%

A composition for inhibiting the accumulation of snow and ice may comprise whey by itself. Alternatively, a composition comprising whey and water may be used. The water content may vary, but preferably, at least 5% by weight of the composition is water. The percentage of whey may also vary. Preferably, there is at least 10%, but most preferably at least 30%, by weight of whey.

Alternatively, the deicing composition comprised of whey may be further admixed with optional additives. These optional additives include skid-reducing agents and conventional chemical deicing agents, such as sodium chloride, calcium chloride, potassium chloride, magnesium chloride, calcium magnesium acetate and urea. The compositions are excellently suited to serve as anti-freeze and deicing agents for inhibiting the accumulation of snow and ice on roads, bridges and other surfaces.

The deicing composition has a freezing point below 0°F. It is liquid and slow flowing at temperatures at least as low as -10°F and may be sprayed and applied to road surfaces or accumulated ice or snow at ambient winter temperatures. The composition may also be heated before its application to facilitate pumping and to enhance the deicing effect.

The deicing composition also serves as a corrosion inhibiting agent when mixed with corrosive salts. Tests have shown that the corrosive effect of an admixture of the composition with a five percent by weight of chloride salts is significantly less than, for example, an admixture of 95 percent water and five percent salts. Thus, a composition comprising whey may be effectively mixed with small amounts of salt without significantly affecting the other characteristics of the composition.

The condensed composition of whey is water soluble, negligibly corrosive, inexpensive, widely-available in large quantities, and effective as a deicing composition. There are no known or identified hazards to humans, animals or the environment from the handling, storing, or using

whey. The composition is a renewable agricultural by-product and its commercial usage may help support U.S. farmers and the agricultural industry.
Beer brewing by-products (Johnson et al., 1999)

The deicing composition is formed from brewers' condensed solubles (BCS). BCS are by-products of a brewing process of grains to create brewed beverages, such as beer, and may be made from any number of grains, including without limitation, corn, wheat and barley.

Deicing compositions may comprise by weight less than 100% BCS as shown in Table 1.9. Compositions may be further admixed with optional additives, such as skid-reducing agents and conventional deicing and anti-freeze compositions.

Table 1.9: Composition of BCS Deicer Fluid

Component	Typical Range		Preferred Range	
	Low %	High%	Low %	High %
BCS	3	95	14	80
Water	5	97	20	86

A 50% BCS soluble-50% water composition has a freezing point below 10°F. It is free flowing at +5°F and can be easily sprayed using conventional spraying equipment upon road surfaces or accumulated ice or snow at ambient temperatures.

A municipality mixed approximately 1/3 sodium chloride with 2/3 sand and added approximately 5% by weight of BCS. The resulting mixture proved more effective than a comparable mixture of salt and sand alone. Thus, the municipality was able to reduce its total annual usage of salt by approximately 25-40%. The resulting mixture also works at lower temperatures than salt alone and can be applied using conventional truck-mounted sand spreader hoppers.

Another municipality mixed approximately 97% chloride salts with approximately 3% BCS. The resulting mixture proved more effective than salt alone. The mixture melted more ice and snow during a fixed period of time and also melted ice and snow at lower temperatures than salt working alone.

BCS are biodegradable, water soluble, negligibly corrosive, inexpensive and widely-available in large quantities. BCS are also safe and possess no undue hazards to humans, animals or the environment from the handling, storing, or use of BCS even when concentrated. The composition is a renewable agricultural by-product, and its commercial usage will help support U.S. farmers and the agricultural industry.

Urea (Kerti et al., 2001)

The deicing composition comprises an aqueous solution of urea and ammonium-nitrate. It has been discovered through experimentation that the most advantageous composition can be attained at the 5:4:7 water--urea--ammonium-nitrate mass ratio. Thus, the aqueous solution has a mass ratio of (4.5-5.5):(3.6-4.4):(6.3-7.7). In addition, 1.5-2.0% mass of benzoic-acid and/or 0.10-0.25% mass of benzo-or tolyl triazol can be added as corrosion inhibitors.

The thermodynamic freezing point of the mixture is -18°C. At this temperature, separation of the chemicals begins. Thus, the liquid is diluted, and its freezing point decreases to -28°C, which is attainable at the 8:4:7 mass ratio. This indicates that the freezing point, in the course of the ice dissolution, is decreased and the rate of the ice-dissolving process is increased. The liquid, having attained the eutectic composition at -28°C, is further diluted and attains the original freezing point of -18°C at the 16.5:4:7 mass ratio. Consequently, the liquid which comprises a 31% water content at 5:4:7 ratio can be diluted as far as 60% water without elevating its original freezing point or reducing its frost resistance.

The density of the mixture produced is 1.26 g/cm^3. The pH of the urea solution produced is in the range of 7.0-7.5. If required, correction can be done with some ammonia or nitric acid. Although the liquid is moderately corrosive, it biodegrades in 2 to 4 weeks, depending on the ambient temperature, which limits the damage to contacting surfaces. The urea solution provides long-lasting protection against renewed icy drizzling, and the acting components of the liquid are also becoming profitable as vegetal nutrients.

Particulate plant material (Koefod, 2000)

The deicing composition consists of a particulate deicer salt and a particulate plant material. The particulate deicer salt is selected from the group consisting of sodium chloride, magnesium chloride, calcium chloride, potassium chloride and mixtures thereof.
The dry ground plant material is selected from the group consisting of dried ground alfalfa, wheat, field and/or lawn grass, linseed, malt, barley, milkweed, clover, vetch, plantain, sorghum, soybeans, canola seeds, carrots, cotton seeds, sunflower seeds, linseed, peanuts, citrus fruits and mixtures thereof. The plant material is ground to a particle size of from about 2000µ (microns) or less and preferably from about 1500µ to about 150µ. The plant material also is dried to a moisture content of about 12 weight percent or less.

The typical composition of the deicing solution is shown below in Table 1.10.

Table 1.10: Composition of Particulate Plant Material Deicer

Component	Typical Range*		Preferred Range*	
	Low %	High %	Low %	High %
Dry, Ground Plant Material	0.5	50	0.5	20
Particulate Deicer Salt	50	99	80	99
Hygroscopic Salt	0.1	0.7	0.3	0.7

** Weight percent based on weight of deicing composition*

The deicer composition consisting solely of dry ground plant material and particulate deicer salt will have a tendency to segregate and not mix well. This will adversely affect the homogeneity of deicer compositions which include sodium chloride and/or potassium chloride. Thus, hygroscopic salts are added to the composition in an amount to bind the particulate plant material to the deicer salt and effect substantial homogeneity in the composition. Adding hygroscopic salts such as magnesium chloride and/or calcium chloride to the deicer composition

will not only pick up water and avoid segregation, but it also will not adversely affect the ability of the deicer composition to deice because of the ability of magnesium chloride and calcium chloride to deice.

The particulate plant material is an inexpensive and naturally renewable material. After grinding and drying, the plant material not only will have a particle size and moisture level which is effective to permit it to be spread by existing commercial equipment which broadcasts existing deicing salts, but the dry, ground plant material will also inhibit the corrosivity of a deicer salt.

Monohydric and polyhedric alcohols (Lockyer et al., 1998)

The anti-icing or deicing composition comprises water, a non-toxic freezing point depressant, a thickener, and an optional corrosion inhibitor. The freezing point depressant is selected from following group of monohydric and polyhydric alcohols: ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, glycerol, and mixtures thereof. The thickener is a xanthan selected to impart viscosity thickening when dispersed or hydrated in the aqueous media.

The typical composition of the deicing solution is shown below in Table 1.11.

Table 1.11: Typical Composition of Decing Composition Containing Monohydric / Polyhedric Alcohols

Component	Typical Range		Preferred Range	
	Low %	High %	Low %	High %
Water*	40	86	40	50
Monohydric/Polyhedric Alcohol*	14	60	50	60
Thickener**	0.01	10	0.25	1.0
Corrosion Inhibitor**	0.01	0.1	0.01	0.1

** Weight percent based on sum of weights of water and freezing point depressant*
*** Weight percent based on total composition weight*

For some applications, it may be desirable to use the anti-icing or deicing composition on a surface, with small grit-sized solid particles, to increase friction and/or traction on the surface. The friction enhancing agents(s) are preferably biodegradable, non-toxic, and non-corrosive in the mixture. Examples of these solids include, pulverized organic nut shells, husks, kernels, seeds, bark, and wood fragments, and certain synthetic polymers, and for selected situations, sand.

The liquid composition can be applied to the surfaces of objects for anti-icing/deicing purposes in conventional equipment.

The deicing composition is an aqueous, non-electrolytic, non-toxic, biodegradable, continuous single phase liquid anti-icing or deicing composition.

Alkalinically reduced sugars (Montgomery et al., 2003)

The deicing composition is formed by alkalinically degrading reducing sugars. The reducing sugars are preferably found in an industrial waste stream, such as corn steep water. Examples of appropriate reducing sugars include glucose, fructose, galactose, ribose, and/or deoxyribose, xylose, arabinose, lactose, and maltose. Glucose and fructose are the preferred reducing sugars for this purpose. Such degraded reducing sugars are effective in increasing the ionic strength and the depression of the freezing point of water without the inclusion of corrosive chloride salts.

The corn steepwater or other reducing sugar source is first treated with an alkali to degrade the reducing sugars into a complex mixture of hydroxy organic acids that consist primarily of lactic acid. Appropriate alkalis for this purpose include divalent and monovalent alkalis. As a general guideline, sufficient alkali should be added to give a final pH of 7-9 after the alkaline degradation reaction of the reducing sugars, with a pH of about 7.0-7.5 being preferred.

The deicing product is effective in lowering the freezing point of water to between about -5°C and -30°C. Studies indicate that the deicing product shows greater freezing point depression when the corn steepwater is treated with protease prior to the alkalinic treatment step. Further, better results are obtained when a monovalent alkali, such as KOH or NaOH is used, rather than a divalent alkali, such as CaO. A significant decrease in freezing point is also seen when from about 20-150 parts by weight in grams of glucose or other reducing sugars are added to 100 parts by volume in milliliters of corn steep water prior to alkalinic degradation. The resulting deicing/anti-icing solution may be used as-is (in liquid form), dried by conventional methods, or freeze-dried and pulverized to a fine powder for more convenient application.

The deicing composition of the present invention may contain other skid-reducing materials as well as other chemical deicing agents. However, the addition of chloride salts negates the biodegradable/non-toxic properties of the composition.

The composition is preferably applied to roads, walkways, sidewalks, airport runways, or other surfaces prior to the accumulation of snow and ice in order to prevent the snow and ice from adhering to the surface. The composition may also be applied to melt existing snow and ice, to prevent further accumulation, and/or facilitate removal. The composition may generally be applied in an amount of 20 to 60 gallons per lane mile, or 0.5 to 1.5 ounces per square yard. However, there is no set upper or lower limit regarding the amount of composition that must be applied to a particular surface.

The deicing composition of this invention offers several advantages over conventional chloride salt-containing deicers. First, the compositions are biodegradable, non-corrosive, and safe for the environment. Further, the compositions may be manufactured from industrial waste from agribusinesses, which is an inexpensive, readily available source.

Succinate salts (Berglund et al., 2001)

It has been determined that succinate salts display both deicing and corrosion inhibiting properties. Succinate salts are both naturally occurring and genetically manufacturable. Deicing compositions comprise of succinate salts, such as potassium succinate (trihydrate), ammonium succinate (anyhdrous), sodium succinate (hexahydrate), or combinations thereof. The following combinations of chemicals may also be added to deicing compositions comprising potassium

succinate in order to enhance the deicing and/or corrosion inhibiting properties of the composition:

- polymaleimide sodium salt and magnesium succinate
- magnesium succinate and sodium polyaspartate
- sodium polysuccinimide
- sodium polyaspartate and polymaleimide sodium salt
- magnesium succinate
- sodium chloride

Applicants determined that potassium succinate repeatedly outperformed other succinate salts. It was found to be an effective deicer and non-corrosive. In comparison to calcium magnesium acetate (CMA), the use of potassium succinate may result in up to a 40% direct savings. Additional indirect savings could be realized on account of the superior deicing capability of potassium succinate. Considering the financial burden incurred by State and County road authorities due to steel corrosion and concrete loss directly as a consequence of road salt use, potassium succinate should prove to be a cost effective, non-corrosive deicer for many of the expensive highway structures. In addition, it may be a viable option for application on environmentally sensitive areas where loss of vegetation and habitat is a concern.

It was determined that many chloride blends containing succinate or succinate-derived corrosion inhibitors displayed performance characteristics that were highly advantageous toward highway deicing. The tested inhibitors were capable of suppressing corrosion induced by the chloride salts as much as 50-75%. This corrosion suppression is advantageous because blends composed of high sodium chloride levels will assist in the development of an affordable product for road deicing applications. In addition, the presence of corrosion inhibitors in small quantities was not found to attenuate the ice-penetration and ice-melting capacities of chloride salts. The net result is a family of cost effective, high-performance deicers that are substantially less corrosive than straight chloride salts.

Alkali metal acetate (Dietl et al., 2005)

The deicing agent consists of an alkali metal acetate, a surfactant, an anti-foaming agent, a corrosion inhibitor, and water. The deicing composition of the invention includes potassium acetate, an alkali metal acetate. Preferred surfactants used are alkyl (poly)glycosides. Their alkyl groups include preferably 8 to 16 carbon atoms. Defoamers used are preferably polysiloxanes, in particular polydialkylsiloxanes, especially polydimethylsiloxanes. Corrosion inhibitors used are preferably alkali metal phosphates, alkali metal borates, and alkali metal silicates.

The composition of the deicing agent is presented below in Table 1.12.

Table 1.12: Composition of Deicing Agent Containing Alkali Metal Acetate

Component	Typical Range		Preferred Range	
	Low %	High %	Low %	High %
Alkali Metal Acetate	45	55	48	52
Surfactant	0.001	1.0	0.02	0.2
Anti-foaming Agent	0.0001	1.0	0.00052	0.01
Corrosion Inhibitor	0.001	1.0	0.01	0.7
Water	Balance		Balance	

The invention further provides a method of melting snow and ice on traffic areas by applying from 5 to 100 g/m^2, preferably from 15 to 80 g/m^2, of the deicing composition of the invention to the traffic area. The amount of deicing composition to be applied depends in particular on the external temperature and on the amount of ice and/or snow present. The deicing composition can be applied using the standard spreading vehicles.

Calcium chloride and urea (Ossian et al., 1997)

A vegetation-friendly ice melting composition with sub-zero ice melting characteristics includes mixing non-fully hydrated ice melter, which is preferably calcium chloride, with fertilizer, which is preferably urea. The most preferred composition is about 70 parts by weight of calcium chloride and about 30 parts by weight of urea. The calcium chloride and urea are preferably admixed first to coat the calcium chloride. To this mixture is added a measured amount of powdered non-fully hydrated calcium chloride as a solid coatant. The non-fully hydrated calcium chloride by hydration forms a coating around the ice melt base. The resultant mixture is discharged from the mixer, screened and packaged.

The composition of the deicing agent is presented below in Table 1.13.

Table 1.13: Composition of Deicing Agent Containing Calcium Chloride and Urea

Component	Typical Range		Preferred Range	
	Low %	High %	Low %	High %
Calcium Chloride	60	90	70	80
Urea	10	40	20	30

The composition is an excellent deicer with favorable abrasion or gripping properties, which also avoids undesirable environmental problems caused by spill or runoff. At the same time, the deicing composition is commercially acceptable in that it has good packaging and free flow properties. The final ice melting composition has excellent ice melting characteristics and limits damage to turf grass while providing a greening effect to vegetation.

Non-chloride based liquid deicer (Seo, 2007)

The deicer composition includes potassium acetate, disodium succinate, dipotassium succinate, ethylene glycol, ethanol, and an aqueous polyvinyl alcohol solution. Potassium acetate lowers the freezing point and acts as a snow/ice melting agent. Disodium succinate serves as an anti-corrosion agent. Dipotassium succinate is a catalytic snow/ice melting agent. Ethylene glycol serves a role in lowering a freezing point. Ethanol lowers a freezing point and serves as a snow/ice melting agent. Polyvinyl alcohol (PVA) acts as a binder for the composition.

The composition by weight of the deicing agent is presented below in Table 1.14.

Table 1.14: Composition of Non-Chloride Based Deicing Agent

Component	Typical Range	
	Low %	High %
Potassium Acetate	10	20
Disodium Succinate	3	10
Dipotassium Succinate	1	5
Ethylene Glycol	5	10
Ethanol	5	15
Polyvinyl Alcohol	40	70

The deicer composition has a freezing point of approximately -15°C to approximately -30°C. Even though lots of moisture is produced on road surfaces as snow/ice melts by the deicer, there may not be an incidence of re-freezing even at the abrupt descending temperature.

The liquid type deicer is not corrosive due to a non-chloride based composition, does not pollute soils, and is not re-frozen. Also, the liquid type deicer can be stored in a liquid state, is cost-effective due to a continuously maintained reaction as the deicer chemicals remain continuously on snow/ice, and can be easily sprayed. Further, the liquid type deicer is capable of removing snow/ice and preventing a re-freezing tendency.

Commercially Available Deicing Agents from Agricultural Products

GEOMELT® (Road Solutions, Inc., 2007)

GEOMELT® anti-icing and deicing fluid is a natural, agricultural product that features ice control performance equal or superior to traditional brines, but less corrosive.

GEOMELT® anti-icing fluid is derived from a renewable sugar beet source and provides a versatile ice control process that is an attractive choice where environmental concerns are important.

GEOMELT® mixes well with traditional brines, natural brines and magnesium chloride and can

be used as stockpile treatment pre-wetting agent and in anti-icing deicing liquid programs. GEOMELT® anti-icing fluid passes the strict specifications of the Pacific Northwest Snowfighters.

Additional advantages to GEOMELT® include:

- Effective to -25° Fahrenheit
- Reduction in full application rates from 30 to 45%
- Reduction in corrosion on bridges, bridge decks and concrete.
- Savings in labor and fuel cost.
- Prevention of bonded ice and hard pack to the road surface.
- Reduction in bounce and scatter of road salt at the spinner

Figure 2.1: GEOMELT® Application

Figure 2.2: Road Clear After GEOMELT® Application

(Both images from www.roadsolutionsinc.com/deicing%20products.htm#geomelt)

Magic Minus Zero™ and Magic Salt™ (MagicSalt.info, 2007)

Magic Minus Zero™ is a highly effective liquid deicing agent made from a patented blend of magnesium chloride combined with an agricultural by-product of the distilling process (i.e., grain and/or sugar based) and is protected under U.S. patent #4,676,918. No other liquid ice melter can make this claim.

Magic Minus Zero™ is non-toxic, bio-degradable and has a corrosion index lower than distilled water.

Figure 2.3: Road Application of Magic Minus Zero™ (www.magicsalt.info)

Magic Minus Zero™ can be applied directly to paved surfaces in advance of a winter storm and the following results will occur:

- Black ice is eliminated.
- Snow and ice will not bond to paved surfaces due to its residual effect.
- It is environmentally friendly.
- It is less corrosive than distilled water.
- It is approved by the Department of Environmental Conservation (DEC).
- It is safe for concrete parking structures.
- It even neutralizes rust.

Figure 2.4: Deicing Results (www.magicsalt.info)

Magic Minus Zero™ is used extensively on the New York State Thruway system and the Garden State Parkway (New Jersey) as an anti-icing agent.

Magic Minus Zero™ can be applied directly to paved surfaces in advance of a winter storm, or can be sprayed onto regular rock salt, transforming it into Magic Salt™, a highly effective ice melting product

Magic Salt™ is regular rock salt that has been treated with the liquid Magic Minus Zero™. Magic Salt™ is safe to use on concrete, is non-corrosive, does not harm curbside grassed areas or plants, and continues to melt ice to below -35F°.

Figure 2.5: Comparison of Vegetation Damage (www.magicsalt.info)

Icenator Liquid Deicer (eHealth Solutions, 2005)

Icenator is a corn-based liquid deicer manufactured in the Midwest from corn grown by American farmers. Icenator has been tested and approved, meeting the standards of the National Association of Corrosion Engineers.

The low freezing point of the liquid melt is approximately –85°F, and the solution does not refreeze. The product is virtually non-corrosive on all surfaces and quickly penetrates ice, frost and snow.

When applied in a stream, the liquid deicer penetrates to break the bond at the asphalt or concrete surface and aids in prevention of the "slickness" period that occasionally occurs with chloride brines. Once dry, asphalt sprayed with Icenator has more traction than asphalt that has not been sprayed at all.

Under the toughest conditions, highway departments and municipalities use the Icenator formula, and it has proven itself over and over again.

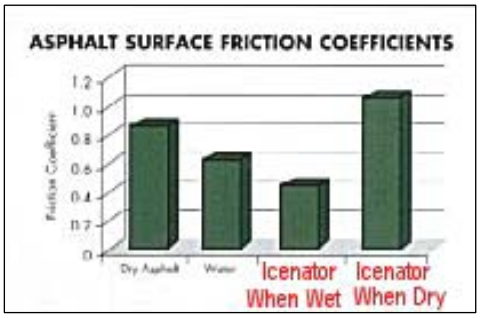

Figure 2.6: Asphalt Surface Friction Coefficients (www.icenator.com)

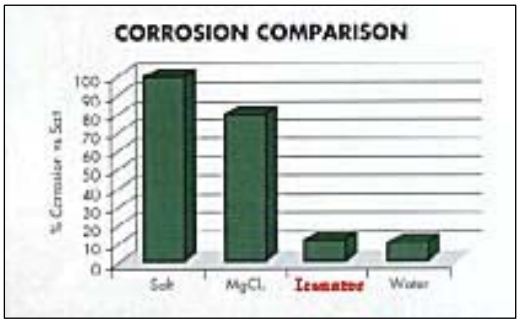

Figure 2.7: Corrosion Comparison of Deicers (www.icenator.com)

Bare Ground Solution (Bare Ground Systems, 2003)

Bare Ground liquid deicer is a patented formula made from all natural by-products of corn processing and magnesium chloride liquid (Unique Idea, 2007). Bare Ground liquid deicer is environmentally safe, bio-degradable, water soluble, virtually non-corrosive, non-staining and non-toxic to plants, pets and livestock.

Bare Ground liquid deicing solution/anti-icing solution can be applied before, during or after an expected snowfall. Bare Ground liquid deicing solution can be used as an anti-icing solution when applied prior to an expected snow event. Bare Ground anti-icing solution will prevent snow and ice from bonding to the surface and reduce the possible accumulation of snow by as much as 2". Bare Ground liquid deicing solution can also be used after a snow storm to melt residual patches of ice and snow quickly and effectively with little or no detrimental effect to pavement.

Bare Ground liquid deicing solution/anti-icing solution is a unique environmentally friendly mix. Bare Ground liquid deicing solution/anti-icing solution is nearly odor free and has a light amber color. A 5 gallon container of Bare Ground will provide coverage of about 5000sq.ft or the equivalent of 250lbs of harmful rock salt.

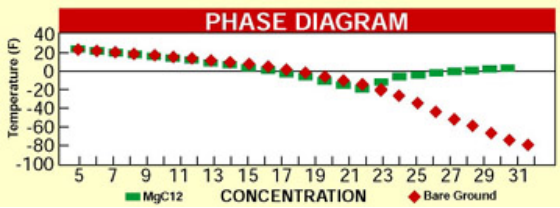

Figure 2.8: Phase Diagram of Comparison Comparison of $MgCl_2$ and Bare Ground Liquid Deicer (www.bareground.com)

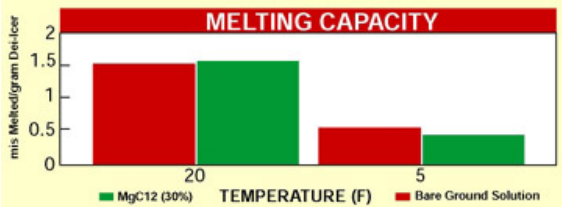

Figure 2.9: Melting Capacity of $MgCl_2$ and Bare Ground Liquid Deicer (www.bareground.com)

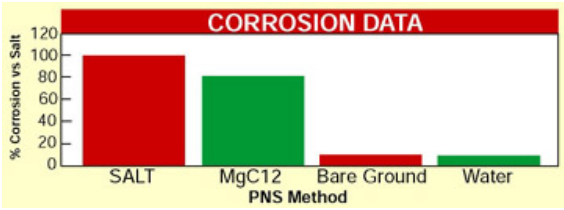

Figure 2.10: Corrosion Comparison of Deicers (www.bareground.com)

Caliber M1000 (Glacial Technologies)

Caliber M1000 is a blend of Caliber deicer with 30% $MgCl_2$. Caliber deicer is derived from corn and is specifically engineered to enhance the eutectic point, anti-icing properties and viscosity of the $MgCl_2$. Additionally, Caliber M1000 also reduces corrosion, inhibits crystal formation and product fallout at lower temperatures, and improves roadway traction when compared to other liquid products.

Caliber M1000 provides a variety of applications in one, non-toxic, cost-effective product. As an anti-icer, Caliber M1000 provides superior "anti-bonding" properties, allowing removal of snowpack with simple plowing. As a liquid deicer, Caliber M1000 provides increased performance vs. other liquid products. When applied in a stream pattern, Caliber M1000 vertically penetrates the snowpack and breaks the bond at the road surface. As a pre-wetting agent for salt and sand, Caliber M1000 reduces bounce and scatter, increases the speed at which the salt begins working, increases the melting capacity of the salt, and permits the use of salt at lower temperatures.

When used for anti-icing operations, application rates of 20-30 gallons per lane mile are typical. These rates can vary depending upon storm conditions and service level goals. As a pre-wetting agent, Caliber M1000 can be used at rates from 5-15 gallons per ton of substrate, depending upon the solid used and the performance objective.

Caliber M1000 deicer passes the test developed by the National Association of Corrosion Engineers Standard TM-01-69 as modified by the Pacific Northwest Snowfighters (PNS). The specification set by the PNS is 70% less corrosive than salt.

Table 2.1: Metal Corrosion Tendency Compared to Rock Salt (NaCl)

Deicing Fluid	Corrosion Rate
Distilled Water	0
Rock Salt (NaCl)	100
Calcium Chloride ($CaCl_2$) @ 38%	121
Calcium Chloride ($CaCl_2$) @ 30%	86
Magnesium Chloride ($MgCl_2$) @ 30%	80
M1000	13.85

Table 2.2: Total Immersion Corrosion per ASTM F483

Test Metal Coupon	SAE AMS 1424 Requirements Wt. Loss ($mg/cm^2/24h$)	M1000 Results
Carbon Steel	0.8 max.	< 0.05
Galvanized Steel	N/A	< 0.75
Aluminum 2024 Anodized	0.3 max.	< 0.01
Aluminum 2024 Alclad	0.3 max.	< 0.01
Aluminum 7075 Alclad	0.3 max.	< 0.01
Copper	Not Established	< 0.01

Table 2.3: Selected M1000 Solution Characteristics

Solids	30% - 33%
$MgCl_2$	26% - 28%
Carbohydrates	4.5% - 5.5%
Specific Gravity	1.28 – 1.32
PH	6.0 – 8.0
Solubility	> 98%
BOD	34,000 ppm
COD	68,000 ppm
Appearance	Clear/Amber
Odor	Slightly Sweet

Table 2.4: PNS Chemical Analysis

	M-1000	PNS Specifications
Arsenic	< 1	5.00 ppm max.
Barium	0.23	10.00 ppm max.
Cadmium	< 0.02	0.20 ppm max.
Chromium	< 0.1	0.50 ppm max.
Copper	< 0.1	0.20 ppm max.
Cyanide	0.09	0.20 ppm max.
Lead	0.57	1.00 ppm max.
Mercury	< 0.01	0.05 ppm max.
Phosphates	0.76	25.00 ppm max.
Selenium	< 1	5.00 ppm max.
Zinc	0.71	10.00 ppm max.

Test Results for Reported Deicing Agents from Agricultural Products

Corn wet-milling by-products (Janke et al., 1999)

Freezing, deicing, and anti-icing

For the tests, mill run steepwater, concentrated at approximately 50% by weight of dry substance, is applied at an external temperature of 14°F to a 3.5 inch thick snow sheet of approximately 20 square yards without any additive. For comparison, a readily recognized and available mixture of industrial salts and sand is applied to a second 3.5 inch thick snow sheet of approximately 20 square yards in a nearby location. It was found that the melting effect of the steepwater composition having a dry substance content of 50% by weight is superior to that of the mixture of salt and sand, both in duration of effect and the strength of activity.

The steepwater composition having a dry substance content of 50% by weight exhibited a melting effect one hour and a half earlier than the mixture of salt and sand. Moreover, the 50% concentration of the steepwater composition is active even at temperatures as low as 7.5°F, while the melting effect of the salt and sand mixture slows and completely stops at approximately 20°F.

Further testing was done utilizing varying concentration of steepwater, varying between 30% and 60% by weight of dry substance, and at various ambient temperatures. Tests were conducted for anti-icing prior to icing, as well as for deicing subsequent to icing. In all cases the results of the steepwater product were equal to superior to the other known, currently used deicing agents.

The following results describe the consistency of a mixture of steepwater concentrated at 48% solids:

Table 3.1: Consistency of Steepwater with 48% Solids at Various Temperatures Below 32°F

Temperature (°F)	Consistency
+20	Free Flowing Liquid
+10	Thin Syrup
0	Thick Molasses
-20	Thick Putty-like

Corrosion

Mild steel bolts were immersed in various concentrations of steepwater. After four months of immersion, the bolts showed virtually no evidence of rust or oxidation. Laboratory corrosion tests measured the corrosive effect at 0.53 mils per year (MPY), which is much lower than any other chemical deicing agent and is a small fraction of the corrosiveness of pure water. A MPY measurement of approximately 13 is generally considered by the deicing industry to be acceptable.

Mild steel bolts were sprayed regularly with various concentrations of steepwater. After four months of regular spraying, the bolts showed virtually no evidence of rust or oxidation. Instead of corroding, the bolts appeared to have been sealed by a layer of dried steepwater, which appeared to be protective rather than destructive.

The following table summarizes some of the test results:

Table 3.2: Steepwater Corrosion Test Results

Material	Corrosion (mils per year, MPY)
Mild Steel	0.53
Stainless Steel	None detectable
Aluminum	None detectable

In comparison, mild steel bolts subjected to similar test conditions as described above, but utilizing mixtures of water and with 5% concentrations of various chloride salts, exhibited extreme corrosion, rust, and deterioration.

Environmental Factors

Tests were performed to measure the biological oxygen demand (in pounds) per pound of various mixtures of the steepwater composition. The BOD represents the metabolic needs of aerobic microorganisms in organic matter. Results appear below:

Table 3.3: BOD Requirement for Steepwater Deicing Solution

Concentration (by weight)	BOD Demand (lb. of O_2 per lb. of material)
25% solids	0.13 – 0.15
48% solids	0.21 – 0.26

The steepwater composition is currently used as a low grade animal feed additive. Because it is widely accepted by the livestock industries and is not known to leave deleterious traces of any harmful substances in the animals being fed, it is believed to be completely safe to the environment and safe to handle as well.

Cheese brewing by-products (Janke et al.,1999)

Freezing, deicing, and anti-icing

For the tests, run-of-the-mill whey, concentrated at approximately 50% by weight of dry substance, is applied at an external temperature of 14°F to a 3.5 inch thick snow sheet of approximately 20 square yards without any additive. For comparison, a readily recognized and available mixture of industrial salts and sand is applied to a second 3.5 inch thick snow sheet of approximately 20 square yards in a nearby location. It was found that the melting effect of the composition having a dry substance content of 50% by weight is superior to that of the mixture of salt and sand, both in duration of effect and the strength of activity.

The whey composition having a dry substance content of 50% by weight exhibited a melting effect one hour and a half earlier than the mixture of salt and sand. Moreover, the 50% concentration of the whey composition is active even at temperatures at least as low as 0°F while the melting effect of the salt and sand mixture slows and completely stops at approximately 20°F.

Further testing was done utilizing varying concentrations of whey, varying between 30% and 60% by weight of dry substance, and at various ambient temperatures. Tests were conducted for anti-icing prior to icing, as well as for deicing subsequent to icing. In all cases the results of the whey product were equal to superior to the other known, currently used deicing agents.

The following results describe the consistency of a mixture of whey concentrated at 50% solids:

Table 3.4: Consistency of Whey with 50% Solids at Various Temperatures Below 32°F

Temperature (°F)	Consistency	Viscosity (SSU)
+20	Free Flowing Liquid	600
+10	Free Flowing Liquid	940
-5	Free Flowing Liquid	1360
-20	Slow Flowing Liquid	2480

Corrosion

Mild steel bolts were immersed in various concentrations of whey. After four months of immersion, the bolts showed virtually no evidence of rust or oxidation. Laboratory corrosion tests measured the corrosive effect at 0.55 mils per year (MPY), which is much lower than any other chemical deicing agent and is a small fraction of the corrosiveness of pure water. A MPY measurement of approximately 13 is generally considered by the deicing industry to be acceptable.

Mild steel bolts were sprayed regularly with various concentrations of whey. After four months of regular spraying, the bolts showed virtually no evidence of rust or oxidation. Instead of corroding, the bolts appeared to have been sealed by a layer of dried whey, which appeared to be protective rather than destructive.

The following table summarizes some of the test results:

Table 3.5: Whey Composition Corrosion Test Results

Material	Corrosion (mils per year, MPY)
Mild Steel	0.55
Stainless Steel	None detectable
Aluminum	None detectable

In comparison, mild steel bolts subjected to similar test conditions as described above, but utilizing mixtures of water and with 5% concentrations of various chloride salts, exhibited extreme corrosion, rust, and deterioration.

Environmental Factors

Tests were performed to measure the biological oxygen demand (in pounds) per pound of various mixtures of the whey composition. The BOD represents the metabolic needs of aerobic microorganisms in organic matter. Results appear below:

Table 3.6: BOD Requirement for Whey Deicing Solution

Concentration (by weight)	BOD Demand (lb. of O_2 per lb. of material)
48% solids	0.23 – 0.25

The whey composition is currently used as a low grade animal feed additive. Because it is widely accepted by the livestock industries and is not known to leave deleterious traces of any harmful substances in the animals being fed, it is believed to be completely safe to the environment and safe to handle as well.

Beer brewing by-products (Johnson et al., 1999)

Test 1
At a temperature of 10°F., a composition of the present invention comprised of 99% of BCS (approximately 48% solubles) and 1% of a surfactant was applied full strength to a 100 ton pile of #1 Crushed Stone. Approximately 10 gallons of the composition of the present invention was sprayed on one side of the pile. Prior to the test, the pile of stone contained frost to a depth of 25 inches. After 24 hours, the composition had penetrated completely through the layer of frost and each stone particle was separated, moving easily when probed with a shovel.

Test 2
Test 1 above was repeated the following day on a pile of #2 Crushed Stone, with similar results. At night the temperature dropped to 6°F, and the following day, tile temperature rose to 22°F. Where the product was applied, the stone material was free flowing. Where the product was not applied, the pile was frozen solid.

Test 3
At a temperature of 22°F, a composition of the present invention comprised 99% of a byproduct concentrate of the beer brewing industry (BCS with approximately 48% solubles) and 1% of a surfactant was sprayed on a pile of road salt. Prior to application, the salt was beginning to form large, hard clumps. The following day, the clumps had completely broken up and the salt was easily stirred and shoveled. The composition of the present invention had no detrimental or dissolving effect on the salt grains and had coated each grain of salt.

Test 4
At a temperature of 22°F, a composition of the present invention was sprayed on an 800 ton pile of manufactured road grit. Prior to application, the grit was encased with a layer of frost about 12 inches deep. The first application penetrated the pile to a depth of about 6 inches. The following day, a second application was made, which penetrated through the frost and made the pile usable without frost clumps.

Test 5
A 2000 ton sand/salt pile was treated with a composition of the present invention. The pile surface was frozen to a depth of about 12 inches, and contained unbreakable frozen ice clumps. Approximately 1000 gallons of composition was sprayed on the surface of the pile and on the frozen clumps. After 24 hours, the pile was free of frost and ice, and was usable for road application. Due to the ability of the composition to break up clumps and dissolve ice, the pile was used and satisfactory deicing results were obtained with 20% less material than would have been required had only sand and salt been used.

Test 6
For the tests, BCS from a brewery, concentrated at approximately 50% by weight of dry substance, was applied at an external temperature of 23°F to an approximately one (1) inch sheet of hard packed snow of approximately 250 square yards without any additives. For comparison, a readily recognized and available mixture of industrial salts and sand was applied to a second one (1) inch thick sheet of hard packed snow of approximately 250 square yards in an adjacent location. Another application of industrial salt with no additional substances mixed in was applied to a third one (1) inch thick sheet of hard packed snow of approximately 250 square

yards in another adjacent location. It was found that the melting effect of the BCS composition having a dry substance content of 50% by weight was superior to that of the mixture of salt and sand, and to that of the salt alone, both in duration of effect and the strength of activity.

The BCS composition exhibited complete melting of the hard packed snow after only about one half hour, while neither of the areas covered by the mixture of salt and sand nor the salt alone was free of snow even after a full hour. Moreover, the 50% concentration of the present invention is active even at temperatures as low as 10°F, while the melting effect of the salt and sand mixture and of the salt alone slows and completely stops at approximately 20°F.

Freezing, deicing, and anti-icing

The following results describe the consistency of a mixture of BCS concentrated at 48% solubles:

Table 3.7: Consistency of BCS with 50% Solids at Various Temperatures Below 32°F

Temperature (°F)	Consistency
+30	30 weight motor oil
+20	30 weight motor oil
+10	Thick molasses
0	Thick, putty-like

The following table summarizes the freezing data and provides quantitative information on a typical mill run BCS solution containing approximately 50% solubles:

Table 3.8: Properties of Typical BCS Solution

Sample Number	Percent Water Added	Percent Solids	Freezing Point (°F)	Specific Gravity	Viscosity @ 70°C (SSU)	Viscosity @ 32°F (SSU)
1	0.0	48	+6	1.240	1600	4000
2	2.1	47	+8	1.234	1350	3700
3	4.2	46	+8	1.228	980	2700
4	16.7	40	+12	1.192	320	1400
5	37.5	30	+18	1.138	100	200
6	58.3	20	+22	1.088	52	60
7	79.2	10	+28	1.042	36	36
8	89.6	5	+32	1.021	35	35

While the melting effect of chloride salts is limited (reduced effectiveness below 30°F, and almost completely ineffective below approximately 20°F), the melting effect of the composition of the present invention, as demonstrated by the tables above, is active even at temperatures as low as 10°F.

Corrosion

Mild steel coupons were immersed in various concentrations of BCS. After four months of immersion, the bolts showed virtually no evidence of rust or oxidation. Laboratory corrosion tests measured the corrosive effect at less than about 0.5 mil per year (MPY), which is much lower than many conventional chemical ***deicing*** agents, and which is well below the requirements of most states. The foregoing corrosion tests were conducted in accordance with National Association of Corrosion Engineers (NACE) Standard TM-01-69 (1976 rev.), as modified by the Washington State Department of Transportation (WSDOT). For comparison, WSDOT specifies that a substance must have a MPY of 13.28 or less to be acceptable. Sodium Chloride typically has a MPY around 44, when measured in accordance with NACE Standard TM-01-69 (1976 rev.).

Mild steel coupons were sprayed regularly with various concentrations of BCS. After four months of regular spraying, the bolts showed virtually no evidence of rust or oxidation. Instead of corroding, the bolts appeared to have been sealed by a layer of dried BCS, which coating appeared to be protective rather than destructive.

The following table summarizes some of the test results:

Table 3.9: BCS Composition Corrosion Test Results

Material	Corrosion (mils per year, MPY)
Mild Steel	0.50
Stainless Steel	None detectable
Aluminum	None detectable

In comparison, mild steel bolts subjected to similar test conditions as described above, but utilizing mixtures of water and with 5% concentrations of various chloride salts, exhibited extreme corrosion, rust, and deterioration.

Environmental Factors

Tests were performed to measure the biological oxygen demand (in pounds) per pound of various mixtures of the BCS composition. The BOD represents the metabolic needs of aerobic microorganisms in organic matter. Results appear below:

Table 3.10: BOD Requirement for BCS Deicing Solution

Concentration (by weight)	BOD Demand (lb. of O_2 per lb. of material)
25% solids	0.13 – 0.17
50% solids	0.28 – 0.32

The BCS composition is currently used as a low grade animal feed additive. Because it is widely accepted by the livestock industries and is not known to leave deleterious traces of any harmful substances in the animals being fed, it is believed to be completely safe to the environment and safe to handle as well.

Particulate plant material (Koefod, 2000)

Corrosion

Standard alfalfa feed pellets (17% protein) are ground to a size range of about 150-1500 μ. Sodium chloride rock salt is blended with 3% by weight of the ground alfalfa.

The corrosivity of the deicer composition is measured by an alternate immersion corrosion test involving the use of 1"x 2" S.A.E. 1010 carbon steel panels which are degreased in hexane and dried after a methanol rinse. The steel panels have a 1/8" diameter hole drilled in the center and near the top of the 1" side. The panels have numbers stamped in each of them. All panels are weighed to the nearest tenth of a milligram after drying. Three percent by dry weight basis of deicer solutions are prepared using the above salt/alfalfa composition in a first solution and plain deicing salt in a second solution. Four panels are suspended in the 3% deicer solutions by threads from a glass rod, such that the panels are completely immersed. During two 1-hour periods each work day, the panels are suspended in air to achieve good contact with oxygen. The other 22 hours of each work day the panels are fully immersed. Over weekends, panels are completely immersed. At the end of each week, old solution is removed and replaced with new solution of the same type. At the end of one month, the panels are removed and the solutions cleaned with 1820 g. hot water, 180 g. of concentrated hydrochloric acid and 2 g. of Rodine 213.

After exposure to the test solutions for 4 weeks, the average corrosion rate in the solution containing the salt/alfalfa composition is found to be 7.3 mils per year, compared to an average corrosion rate of 18.0 mils per year in the solution of plain sodium chloride.

Ice Melting Capabilities

Ice melting capacities of a deicing composition and of plain sodium chloride are compared. A mixture of sodium chloride rock salt with 3% ground alfalfa and 1.75% magnesium chloride solution (containing 30% magnesium chloride by weight) is applied to ice at 15°F, and the volume of ice melted is measured after 60 minutes. This procedure is repeated using plain rock salt.

Plain salt yields 13.8 milliliters of melt (standard deviation=2.8).
The salt/alfalfa composition yields 13.2 milliliters of melt (standard deviation=1.6).

Alkalinically reduced sugars (Montgomery et al., 2003)

Determination of Freezing Point

EXAMPLE 1:

44 g of glucose and 19.55 g of NaOH were dissolved in 200 mL of water and heated with stirring at 100°C for 2 hours. The resulting degradation products were diluted or concentrated in a rotary evaporator and analyzed for the respective freezing temperatures. Degradation products of glucose by different alkali were also prepared using KOH (27.4 g) or CaO (12.4 g). These results are summarized in Figure XX. Aqueous solutions of NaCl, $CaCl_2$ and sodium gluconate (GlcA-Na) were included for comparison (inset).

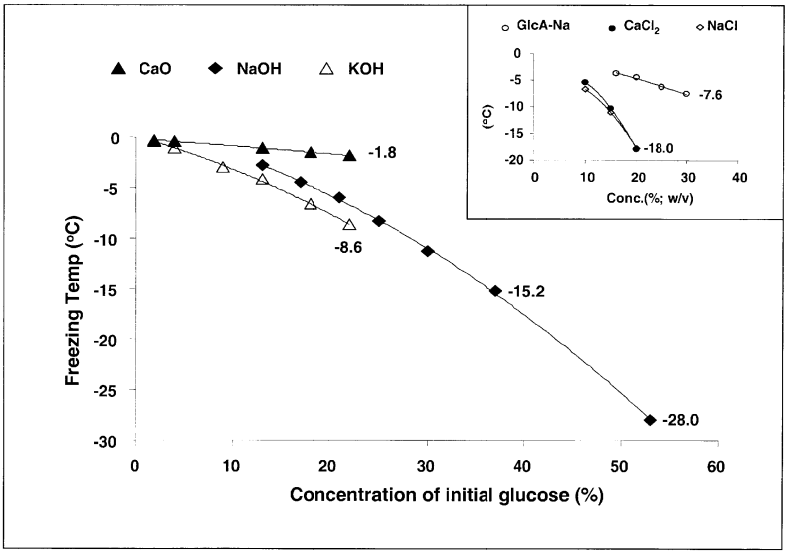

Figure 3.1: Freezing Temperature of Alkalinically Reduced Glucose (http://patimg1.uspto.gov/.piw?docid=US006605232&PageNum=2&IDKey=30BCC0E4416F&HomeUrl=)

EXAMPLE 2:

Corn steep water (100 mL) was mixed with water-soluble proteases (1.0 g) of Aspergillus oryzae (Pro1) or Aspergillus niger (Pro2) and incubated at 50°C for 24 h. The resulting solution was adjusted to pH 6 with 2.5 mL of 10 M KOH (or equimolar amounts of NaOH) and incubated further at 50°C for 24 h with or without bacterial amylase (amyl) from B. subtilis (0.2 mg). The resulting solution was adjusted to pH 12.5 with 9.2 mL of 10 M KOH (or equimolar amounts of NaOH) and heated at 100°C for 2 h, or 85° C for 45 minutes, with n-octanol (100 .mu.L) as a de-foaming agent. The freezing point of the resulting solution was determined directly and summarized in Figure XX. The effect of various treatments to the corn steep water was also included for comparison.

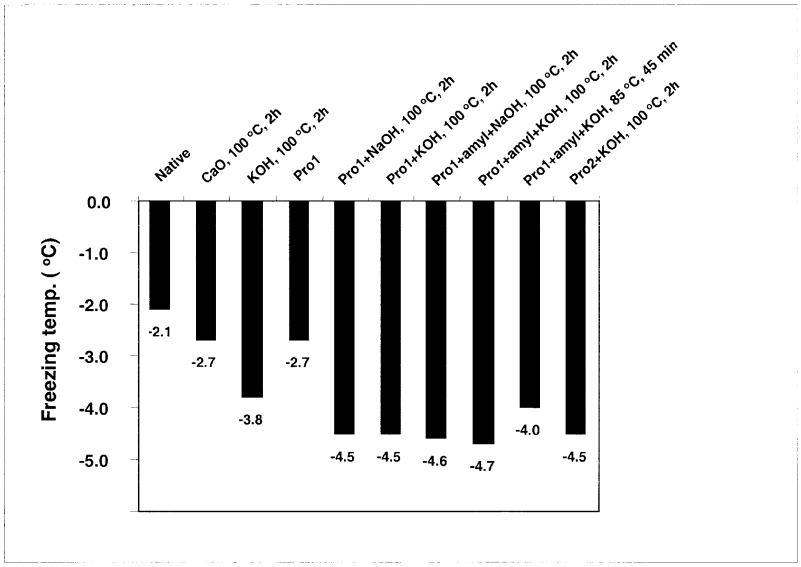

Figure 3.2: Freezing Temperature of Treated Corn Steep Water (http://patimg1.uspto.gov/.piw?docid=US006605232&PageNum=3&IDKey=30BCC0E4416F&HomeUrl=)

EXAMPLE 3:

Corn steep water (200 mL) was mixed with water-soluble proteases (2.0 g) of Aspergillus oryzae and incubated at 50°C for 16 h. The resulting solution was adjusted to pH 12.5 with 10 M KOH (18.4 mL) and heated at 100°C for 2 h with n-octanol (200 μL) as a de-foaming agent. The insoluble materials (small amount) were removed by centrifugation, and the resulting supernatant was appropriately reduced in rotary evaporate (45°C.) and analyzed for the freezing point. The results against the extent of concentration from the initial volume are summarized in Figure XX.

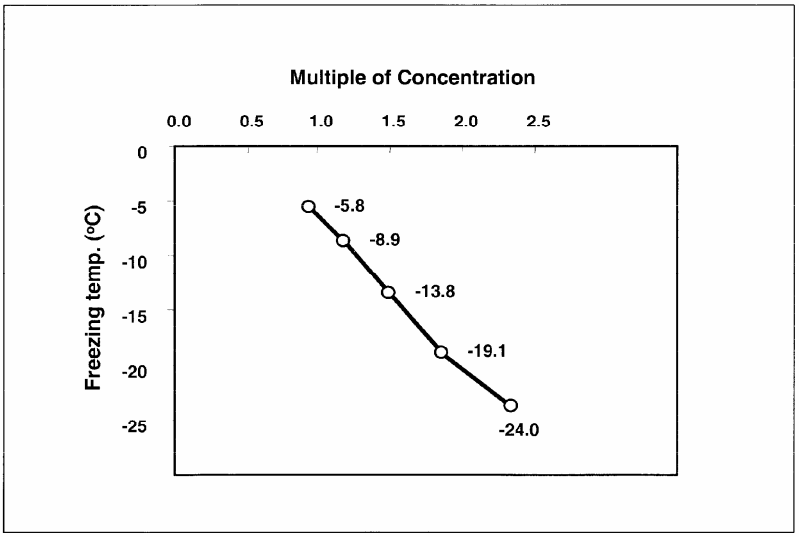

Figure 3.3: Freezing Point of Treated Corn Steep Water at Various Concentrations (http://patimg1.uspto.gov/.piw?docid=US006605232&PageNum=4&IDKey=30BCC0E4416F&HomeUrl=)

EXAMPLE 4:

The protein from corn steep water (100 mL) was precipitated by adjusting pH to 7.0 with NaOH of 1.44 g. The supernatant was recovered by centrifugation (9800 g, 30 min) and mixed with glucose of 20 g and NaOH of 7.4 g and then heated at 81°C for 1-2 hours. The resulting solution showed a freezing temperature of -10°C to -11°C.

EXAMPLE 5:

44 g of glucose and 19.55 g of NaOH were dissolved in water of 200 mL and heated with stirring to 100°C for 2 hours. The resulting reaction solution was freeze-dried and further dried in a high vacuum desiccator (60°C, 24 h) before pulverization. The resulting solid materials were dissolved in the supernatant of corn steep water at pH 7, as described in Example 4, or the protease-digested corn steep water, as described in Example 3. The freezing temperatures of the resulting solutions are summarized in Table 3.11, together with NaCl for comparison.

Table 3.11: Freezing Point of Alkalinically Reduced Glucose Dissolved in Treated Corn Steep Water at Various Concentrations

Concentration % (w/v)*	Freezing Temperature (°C)			
	CSW 2 (Example 4)		CSW 1 (Example 3)	
	Glc-NaOH	NaCl	Glc-NaOH	NaCl
10	-5.6 ± 0.4	-10.3 ± 0.1	-5.6 ± 0.2	-11.3 ± 1.4
15	ND	-13.3 ± 1.1	-7.4 ± 0.1	-15.5 ± 1.0
20	-8.8 ± 0.6	-18.1 ± 0.5	-9.8 ± 0.3	-19.6 ± 1.0
23	ND	-21.0 ± 0.1	ND	-21.5 ± 1.5
25	-12.1 ± 1.2	ND	-11.4 ± 0.0	ND
30	-12.9 ± 0.9	ND	-13.4 ± 1.0	ND

**Concentration of reaction solids or NaCl in parts by weight in grams and CSW in parts by volume in milliliters ND: not determined*

EXAMPLE 6:

Glucose (100 g) was dissolved in corn steep water (50 mL) at 60°C. n-octanol (500 µl) was added to reduce any foaming, followed by KOH (34.36 g) in three portions and with stirring. The resulting solution was maintained at 60°C for 16 h. The resulting product was appropriately diluted with water and analyzed for freezing temperature, viscosity and specific gravity (Table 3.12). These results are summarized together with the soluble solid content (dried in high vacuum desiccator, 60°C, 24 h) in the resulting solution. Data for ethylene glycol was included for comparison.

Table 3.12: Properties of Alkalinically Reduced Glucose in Corn Steep Water Solution

Dry Weight % (w/w)	Freezing Temp. (°C)	Viscosity (cp)			Specific Gravity (g/ml)
		20°C	5°C	-8°C	
52.8	-26.6	13.4	18.2	54.2	1.273
56.2	-29.3	20.4	43.1	90.8	1.298
59.3	-29.3	31.5	72.5	91.7	1.315
65.7	NC*	62.8	237.7	615.5	1.360
Ethylene Glycol		18.9	40.9	76.1	1.112

** NC = no crystallization observed*

Succinate salts (Berglund et al., 2001)

Method for the Determination of Ice-penetrating Capacity of Deicers

As described below, a slightly modified version of the SHRP H-205.3 protocol of the "Handbook of Test Methods for Evaluating Chemical Deicers", SHRP-H/WP-90, Strategic Highway Research Program, National Science Counsel, Washington, D.C., (1992)" was followed. The ice-penetration capacity was measured based on an observation of the penetration behavior of the

deicer, which occurs chiefly by the propagation of a uniform melt front downward through the ice. The test involved the following steps:
1. Distilled water was placed in standard ice-penetration test cells and frozen.
2. Deicer samples of 25 mg or 100 mg were stored at room temperature.
3. The deicers were placed on the ice in the test cell at preset temperatures of -5°C, -10°C, -15°C and -20°C.
4. At regular intervals of 10, 20, 30, 45 and 60 minutes, the ice-penetration depth was measured. The penetration depth was observed with the aid of a drop of dilute Bulls-Eye® dye placed on the ice surface. The dye gives a distinctive blue color at the ice-penetration front.
5. Tests were performed in triplicate.

Method for the Determination of Steel and Aluminum Corrosion Properties

The evaluation of corrosion inhibition properties, the SHRP H-205.7 protocol of the "Handbook of Methods for Evaluating Chemical Deicers", incorporated herein by reference, was followed. Corrosion properties of the numerous deicers were evaluated using 3% wt aqueous solutions. The test protocol involved the following steps;
1. Seven hundred and fifty milliliters of aqueous salt solutions was placed in stoppered Erlenmeyer flasks. The stopper was intended to prevent the rapid evaporation of water while permitting aeration for accelerated corrosion under controlled conditions. Metal coupons (SAE 1010 steel and ASTM D1730 aluminum), 1"x 2", were suspended in the solutions with the aid of nylon string tied to a hole in the coupon.
2. The metal coupons were subjected to accelerated corrosion for two weeks while monitoring airflow, solution level, solution color and solution pH.
3. The corrosion rate, in mpy (1/1000 inches per year), was determined using the SHRP H-205.7 protocol for steel and aluminum.

Method for the Determination of Magnesium Corrosion Properties

For the evaluation of corrosion inhibition properties the ASTM F 483-91 protocol of the "Standard Test Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals", incorporated herein by reference, was followed. Corrosion properties of the numerous deicers were evaluated using 3% wt aqueous solution. The test protocol involved the following steps;
1. 450 milliliters of aqueous salt solutions were placed in stoppered Erlenmeyer flasks. The stopper was intended to prevent the rapid evaporation of water. The solutions were kept at 38°C during 24 hours of experimentation. Metal coupons (Dichromate treated as in AMS 2475 Wrought Magnesium alloy designated as ASTM AZ31B to AMS 4376.), 1"x 2", were suspended in the solutions with the aid of nylon string tied to a hole in the coupons.
2. The metal coupons were subjected to corrosion for 24 hours while monitoring solution level, temperature, color and pH.
3. The corrosion rate, expressed in mg/cm^2, was determined using ASTM F 483-91 protocol.

Method for the Determination Freezing Points

The following protocol was followed to determine the freezing points of deicers. Deicer concentration in aqueous media was 50% wt.

1. Eight milliliters of aqueous deicer solutions were placed in sealed, plastic tubes.
2. The tubes were immersed overnight in a Polystat Chiller containing silicone heat transfer fluid maintained at predetermined temperatures. The temperature range was
0°C to -45°C.
3. After the overnight immersion period, the deicer samples were visually examined to identify the frozen ones and recorded.
4. The temperature was further lowered and the samples remaining in a liquid state were kept immersed overnight.
5. Steps 3 and 4 were repeated until all samples in an experiment were frozen.

Potassium Succinate vs. Calcium Magnesium Acetate (CMA)

EXAMPLE 1:
First, the performance of substantially pure solid potassium succinate was compared to that of CMA to demonstrate the overall superiority of potassium succinate as a non-corrosive deicer with respect to ice penetration capacity and corrosion characteristics.
The ice-penetration performance of potassium succinate and CMA are presented in Figure 3.4. The protocol described earlier (Method For The Determination of Ice-Penetrating Capacity of Deicers) was used with 25 mg of solid deicer. The rate of ice-penetration of CMA at -5°C and -10°C is significantly lower than that of potassium succinate. Calcium magnesium acetate was totally ineffective below -10°C. Clearly, potassium succinate was shown to be a superior deicer compared to CMA at temperatures down to -20°C and does not freeze until its temperature drops below -40°C.

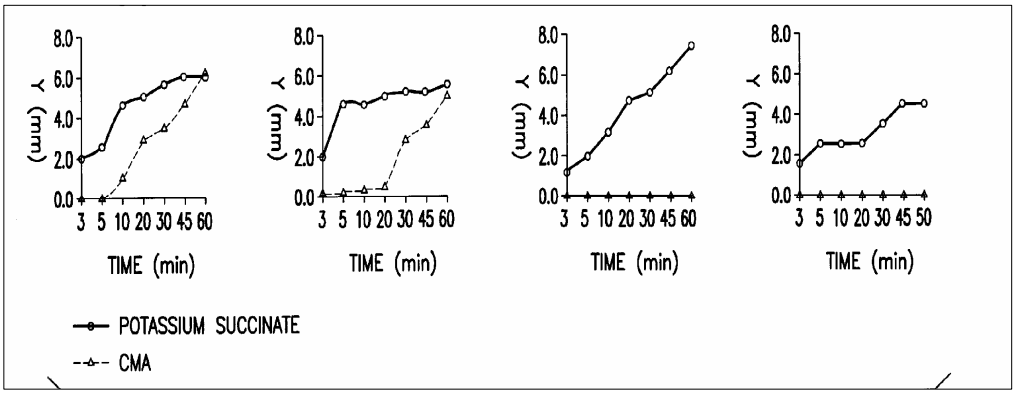

Figure 3.4: Ice-penetration Capacity of Potassium Succinate and Calcium Magnesium Acetate
(http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=2&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

EXAMPLE 2:
The steel corrosion rates in 3% wt aqueous solutions of potassium succinate, CMA and sodium chloride were evaluated. The results indicate that both potassium succinate and CMA do not promote significant steel corrosion. The rate of steel corrosion in potassium succinate and CMA was 0.01 mpy and 0.04 mpy, respectively. These negligible values would fall into experimental error limits. This is confirmed by the observation that no corrosion appeared on metal samples in repeated experiments. Conversely, the steel corrosion rate in sodium chloride was 18 mpy, and corrosion was visible.

EXAMPLE 3:
The inhibition of steel corrosion by potassium succinate and CMA in aqueous sodium chloride solutions were evaluated. The added potassium succinate and CMA was 2% wt of the total amount of salt while the total amount of salt was 3% wt of the aqueous solution. The results of this experiment are presented in Figure 3.5. As shown, small amounts of either potassium succinate or CMA have a significant impact on the corrosiveness of sodium chloride. Both potassium succinate and CMA inhibited more than 50% of the corrosion induced by sodium chloride.

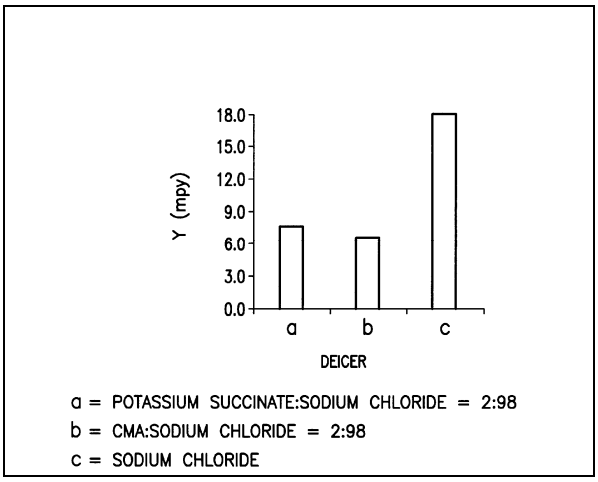

Figure 3.5: Steel Corrosion Rates for Potassium Succinate and CMA in Aqueous Sodium Chloride Solution (http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=3&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

Potassium Succinate vs. Other Succinate Salts

EXAMPLE 4:
The performance of potassium succinate was compared to that of other succinate salts. The succinate salts included sodium, ammonium, calcium and magnesium succinate.
The SHRP H-205.3 protocol of the "Handbook of Methods for Evaluating Chemical Deicers" for evaluating ice-penetration capacity of deicing chemicals suggests the use of 25 mg of deicer in a test cell. However, 100 mg of deicer was used based on the respective anhydrous species to accentuate the subtleties, if any, in the performance of the salts tested. Therefore, the absolute ice-penetration depths of potassium succinate presented in Figure 3.4 (Example 1) differs from that presented in Figure 3.6.

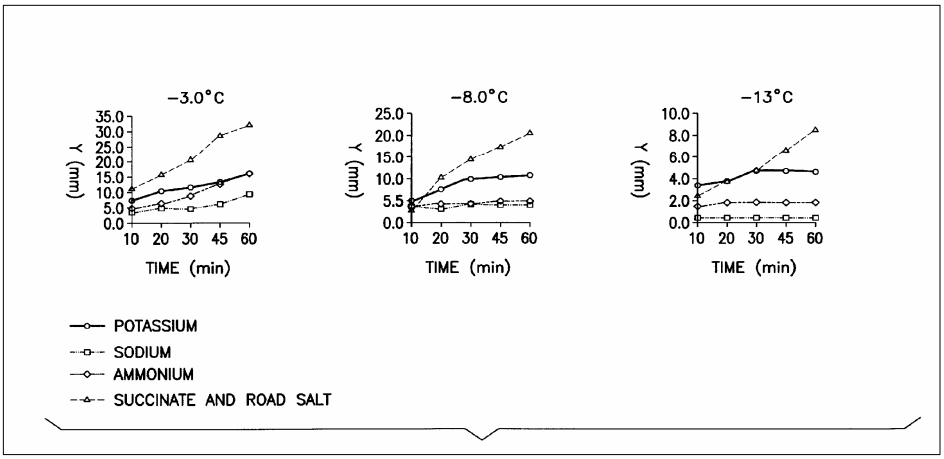

Figure 3.6: Ice-penetration of Various Succinate Salts (http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=4&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

EXAMPLE 5:

The synergistic effects of these salts were also examined. Ice-penetration tests were carried out using 50:50 mixtures of potassium succinate (trihydrate), ammonium succinate (anhydrous) and sodium succinate (hexahydrate). The components were measured on an anhydrous basis. The results are presented in Figure 3.7.

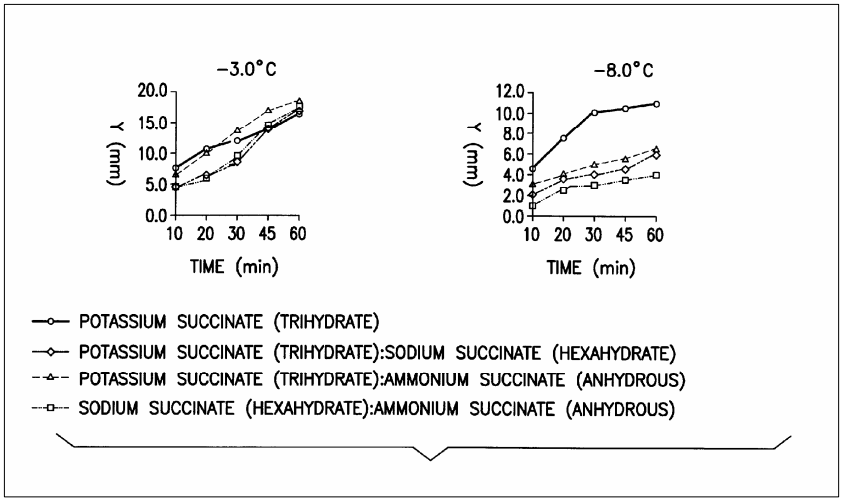

Figure 3.7: Ice-penetration of 50:50 Succinate Salt Mixtures (http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=5&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

EXAMPLE 6:

The steel corrosion rate in 3% wt aqueous solutions of potassium succinate, sodium succinate, ammonium succinate and sodium chloride was studied. The results presented in Figure 3.8 indicate that the succinate salts, with the exception of ammonium succinate, do not promote steel corrosion. The rate of steel corrosion in potassium succinate and sodium succinate was 0.01 mpy and 0.03 mpy, respectively. Therefore, the values are not visible on the chart. It is believed that

these negligible values would fall into experimental error limits. This is confirmed by the observation that no corrosion appeared on metal samples in repeated experiments.

The SHRP H-205.7 protocol of the "Handbook of Methods for Evaluating Chemical Deicers" that was used to evaluate corrosion properties of the salts, calls for the suspension of two steel coupons in aqueous deicer solutions. The electrochemical properties of ammonium succinate facilitate extensive corrosion of one of the coupons and protect the other from any corrosion. Ammonium succinate displayed this behavior in repeated experiments. The method used by the protocol to report the data is the average rate of corrosion of the two suspended coupons. For ammonium succinate, the average, as given in Figure 3.8, is 17.13 mpy. This average corrosion rate is reflective of one steel coupon that corroded as much as 34.26 mpy and one that corroded 0.0 mpy.

The aluminum corrosion rate in 3% wt aqueous solutions of potassium succinate, sodium succinate, ammonium succinate and sodium chloride was studied and the results are presented in Figure 3.9. The results indicate that both potassium succinate and sodium succinate do not promote aluminum corrosion. The rate of aluminum corrosion in potassium succinate and sodium succinate was 0.00 mpy and 0.05 mpy, respectively. These negligible values, are believed to fall into experimental error limits. This is confirmed by the observation that no corrosion appeared on metal samples in repeated experiments. Conversely, the aluminum corrosion rate in sodium chloride was 5.4 mpy. The rate of aluminum corrosion in ammonium succinate solutions was 0.5 mpy. Although aluminum corrosion rate in ammonium succinate solutions is higher than that in potassium and sodium succinate solutions, it is substantially lower than that in sodium chloride solutions.

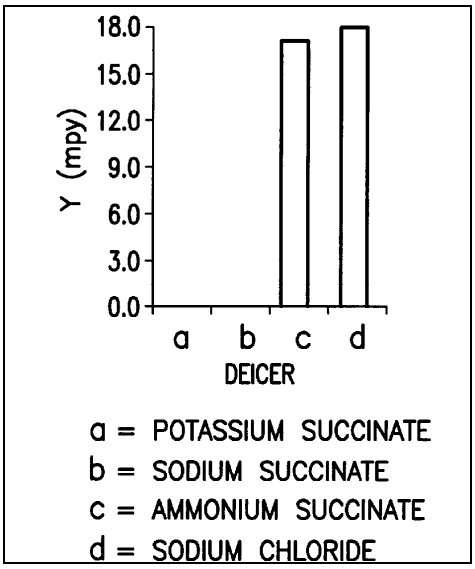

Figure 3.8: Steel Corrosion Rate of 3% Wt Aqueous Solutions of Succinate Salts and Sodium Chloride

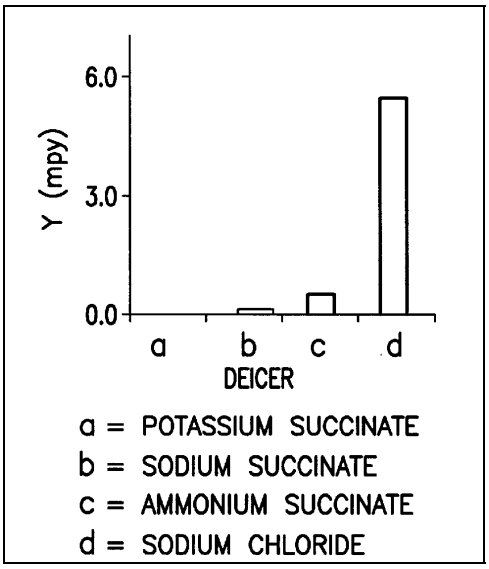

Figure 3.9: Aluminum Corrosion Rate 3% Wt Aqueous Solutions of Succinate Salts and Sodium Chloride

(http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=6&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

EXAMPLE 7:
The inhibition of steel corrosion by potassium succinate, sodium succinate and ammonium succinate in aqueous sodium chloride solutions was studied. The amount of succinate in the chloride blends was 2% by weight (% wt) of deicer. The aggregate amount of deicer was 3% wt of the aqueous solution. Results of these experiments are presented in Figure 3.10.

All three succinates displayed inhibition of chloride induced corrosion in excess of 50%. Thus, formulations inhibiting corrosion by at least 20% or higher (or lower, for that matter) are also possible. This data suggests that the succinates possess corrosion inhibition capabilities in addition to being noncorrosive.

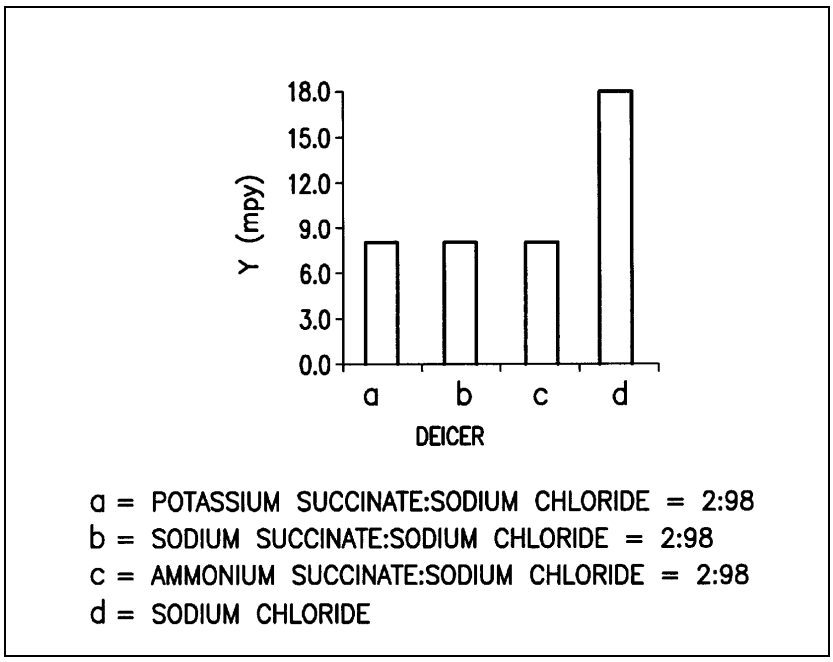

Figure 3.10: Steel Corrosion Rates for Succinate Salts in Aqueous Sodium Chloride Solution (http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=7&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

Scaling Effect of Different Salt Solutions on Concrete Specimens

EXAMPLE 8:
The following experiment evaluates the scaling effect of different salt solutions on concrete specimens.

To measure the scaling effect of different deicing chemicals on concrete surfaces, the SHRP H-205.9 test protocol entitled "The Method for Evaluation of Scaling Effects of Deicing Chemicals on Concrete Surfaces" from the Handbook of Test Methods for Evaluating Chemical Deicers, Strategic Highway Research Program, National Research Council, Report number SHRP-H/WP-90, along with applicable ASTM standards were followed.

Concrete specimens (6x12x3 inches), two for each salt sample, were prepared in specially made molds for each sample. Concrete was supplied by a local concrete mixer. After two stages of 24 hrs (23°C ± 1.7°C at 45 to 55% relative humidity) and 28 days (14 days at 100% relative humidity according to ASTM C 511-85 and 14 days at 23°C ± 1.7°C and 45 to 55% relative humidity) curing process, the specimens underwent 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 cycles of freezing/thawing at a controlled temperature of -17.8°C ± 2.3°C and a relative humidity of about 35%, with thawing at room temperature. At the end of each five cycles, the salt solutions along with scaled concrete were collected from the reservoir or the pond of the specimens. The solutions were vacuum filtered and the residual solids were dried over night and weighed to determine the quantity of scaled material.

The experimental results are presented in Figure 3.11.

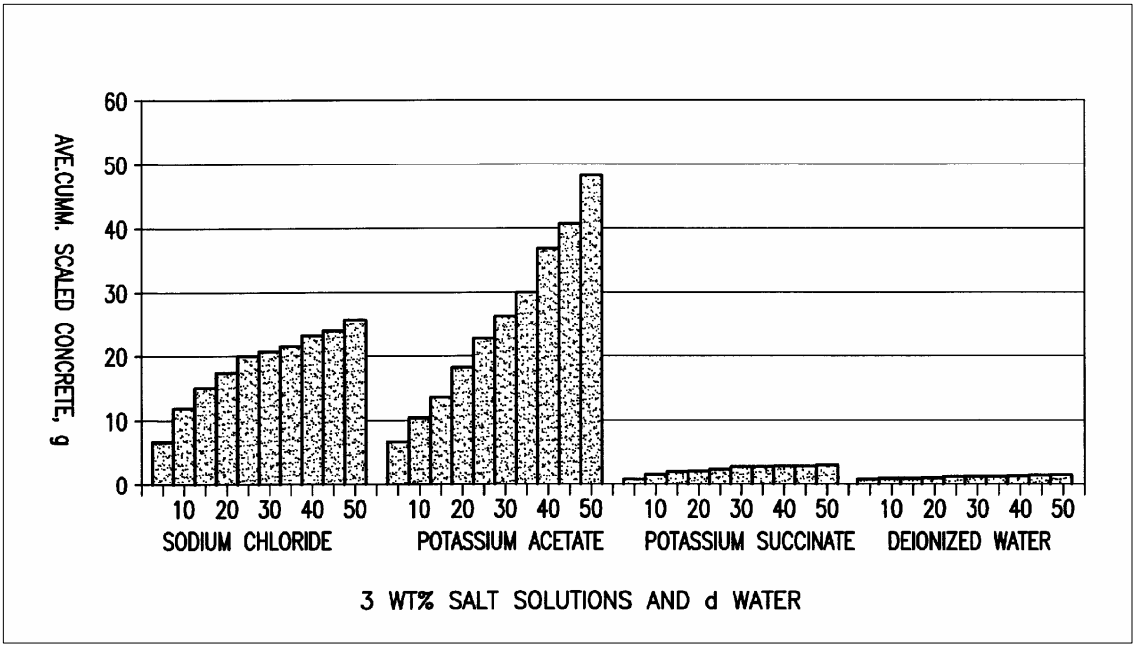

Figure 3.11: Scaling Effect of Various Deicing Chemicals (http://patimg2.uspto.gov/.piw?docid=US006287480&PageNum=11&IDKey=6A17E43ADCEF&HomeUrl=http://www.uspto.gov/patft)

Alkali metal acetate (Dietl et al., 2005)

The icing prevention time was determined in analogy to ISO 11078 at the particular air temperature and concrete slab temperature indicated. In this case, however, icing was carried out using not electropolished aluminum sheets but instead concrete slabs measuring 25 cm x 25 cm x 5 cm with an inclination angle of 1°. 1.857 g of the specified deicing compositions were applied to the slabs, corresponding to an application rate of 30 g of deicer/m^2. The measure used for the icing prevention time is a period of time until the concrete slab starts to ice up.

Table 3.13: Icing Prevention Time for Various Potassium Deicing Solutions

Sample	Temperature (°C)	Deicer	Irrigation Rate ($g/(dm^2\ h)$)	Icing Prevention Time (min)
1	-5	E*	5.8	26
2	-5	E	7.4	19
3	-5	E	8.3	14
4	-15	E	8.1	13
5	-15	E	8.6	14
6	-15	E	9.4	9.5
7 (comp.)	-5	Potassium formate	5.5	22
8 (comp.)	-5	Potassium formate	7.6	12
9 (comp.)	-15	Potassium formate	8.4	10
13 (comp.)	-15	Potassium acetate	8.9	7.5

** E = inventive deicing composition, consisting of a 50% strength by weight aqueous solution of potassium acetate with 0.1% by weight C_8 to C_{16} alkyl glycoside, 0.005% by weight polydimethylsiloxane, and 0.3% by weight K_3PO_4.*

Calcium chloride and urea (Ossian et al., 1997)

The data below for samples 1-16 test the performance characteristics of the product. To do this, several of the samples were placed in a lab freezer at +15°F for one hour. The samples consisted of ice that was prefrozen in plastic cylinders. The amount of ice melter placed in each of the cylinders was calculated to simulate actual usage rates.

At the end of one hour the amount of melted material was poured off and measured. The samples were repeated four times, and the average melting ratios were compared. For example, if one gram melted one gram of liquid brine in one hour, the melting ratio would be one.

The average temperature of +15°F was used, as fertilizers will not melt at this temperature. The results of these comparisons follow:

Table 3.14 below shows best results with urea, or urea blended with calcium chloride and urea coated with calcium chloride solid coating agent.

Table 3.14: Melting Ratio of Various Combinations of Urea and Calcium Chloride

Sample No.	Sample Description	Melting Ratio
1	Urea only	0.0
2	25% calcium chloride	1.1
3	25% calcium chloride, 75% urea (physical blend)	1.3
4	12% coating of calcium chloride onto urea	1.3
5	22% coating of calcium chloride onto urea	1.6
6	25% coating of calcium chloride onto urea	1.7
7	28% coating of calcium chloride onto urea	1.9

A review of the results would indicate that as the calcium chloride ratio is increased, the melting ratio is increased.

Table 3.15: Melting Ratio of Potassium Chloride with Various Concentrations of Calcium Chloride Coating

Sample No.	Sample Description	Grams Melted per Unit
8	Potassium chloride only	0.00
9	7.4% coating of calcium chloride onto potassium chloride	0.22
10	15.3% coating of calcium chloride onto potassium chloride	0.84

A review of the results would indicate that as the calcium chloride ratio is increased, the melting ratio is increased.

Table 3.16: Melting Ratio of Sodium Chloride with Various Concentrations of Calcium Chloride

Sample No.	Sample Description	Grams Melted per Unit
11	Sodium chloride only	1.42
12	7.7% coating of calcium chloride onto sodium chloride	2.02
13	13.7% coating of calcium chloride onto sodium chloride	2.15

The melting characteristics of the formulation 30% urea+70% calcium chloride manufactured by utilizing the preferred coating technique was compared to other traditional ice melters. The comparisons were made at 5°F for 20 minutes and the results are set forth in Table 3.17:

Table 3.17: Melting Performance of 30% Urea + 70% Calcium Chloride and Other Traditional Ice Melters

Composition	Milliliters of Melt
30% urea + 70% calcium chloride	6.8
Potassium chloride	0.0
Urea	0.0
Rock salt (sodium chloride)	1.5
Safe Step® (50% salt + 50% KCl)	1.2

Non-chloride based liquid deicer (Seo, 2007)

Approximately 55 g of aqueous PVA solution with approximately 0.01% w/w was placed into an agitator and was then agitated. Approximately 19 g of potassium acetate was added thereto and was agitated together. Next, approximately 5 g of disodium succinate was added and was then agitated, being followed by an addition of approximately 2 g of dipotassium succinate. The resulting composition was agitated again. Approximately 10 g of ethylene glycol was added and agitated and afterwards, approximately 9 g of ethanol was added and agitated together. These sequential addition and agitation procedures provide a composition for a liquid type deicer, which dose not contain chloride ions and is less corrosive.

Other various exemplary compositions for a liquid type deicer are possible according to other specific embodiments. Table 3.18 provided below shows detailed description of amounts of composing chemicals of such liquid type deicer which is manufactured by the above described method in the first exemplary embodiment.

Table 3.18: Composition of Embodiment and Comparison Samples of Non-chloride Based Liquid Deicers

Sample	Aqueous PVA Solution (g)	Potassium Acetate (g)	Disodium Succinate (g)	Dipotassium Succinate (g)	Ethylene Glycol (g)	Ethanol (g)
Embod. 1	55	19	5	2	10	9
Embod. 2	50	15	5	5	10	15
Embod. 3	55	15	5	5	10	10
Comp. 1	60	10	0	5	20	5
Comp. 2	70	10	5	5	10	0

Those various compositions for a liquid type deicer obtained from the above first to the third embodiments and the first to the second comparison examples are compared with calcium chloride ($CaCl_2$) which is a conventional deicer. Evaluation particulars and methods are described in detail hereinafter.

(1) Corrosive Characteristic
Approximately 10 ml of each sample was placed into approximately 50 ml vials and each lid of vials was opened to provide an air-pathway. A usual silvery white clip was placed into each vial such that approximately 2/3 of each clip was merged into the sample and then, it was checked when corrosion occurred at each clip for the corrosion comparison purpose. Herein, a sample of $CaCl_2$ was an aqueous solution of approximately 25% by weight.

(2) Environmental Friendliness
Those samples were set to have approximately 5% by weight and toxicity of these samples was tested on fish. Especially, longevity values of healthy loaches when using the conventional $CaCl_2$ deicer and the deicers introduced by the above described embodiments were measured for the comparison purpose.

(3) Cost-Effectiveness
A reagent was estimated in the unit of kilograms (Kg) for the individual composition ratio of each sample, and the estimation results were compared with the conventional $CaCl_2$ solution.

(4) Reaction Time (Snow/Ice Removing Effect)
Approximately 50 ml of each sample was placed into individual beakers of approximately 100 ml and then, approximately 9 ml of ice was put thereinto and a time taken for the complete melting of ice was measured. Approximately 25 g of solid $CaCl_2$ was used.

The above described test results are summarized in Table 3.19 below.

Table 3.19: Characteristics of Embodiment and Comparison Samples of Non-chloride Based Liquid Deicers and Calcium Chloride

	Embodiment			Comparison		Calcium Chloride
	1	2	3	1	2	
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Solid
Corrosiveness	65 days	55 days	55 days	30 days	60 days	2 days
Environmental Friendliness	10 days	8 days	9 days	7 days	10 days	1 day
Cost-Effectiveness*	450 wons/kg	450 wons/kg	450 wons/kg	400 wons/kg	300 wons/kg	400 wons/kg
Reaction Time (Snow/Ice Removing Effect)	About 3 minutes	About 3 minutes	About 3 minutes	About 4 min 15 seconds	About 4 minutes	About 5 minutes

100 won ≈ $0.10 USD

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APPENDIX B. INTERNAL IOWA DOT SPECIFICATIONS FOR SELECTION OF DEICER MATERIALS

Iowa Department of Transportation

DEICING CHEMICAL TESTING AND EVALUATION

Any evaluation of a deicing chemical proposed for use by the Iowa Department of Transportation will be subject to a well-defined, multi-step evaluation process. In summary, the process includes:

- Pre-qualification
- Laboratory Testing
- Operational Testing
- Evaluation and Recommendation

PRE-QUALIFICATION

A manufacturer, distributor or supplier shall provide the following information for any deicing chemical, mixture of deicing chemicals or additives/treatments for deicing chemicals.

- **Product literature -** product characteristics, including storage and handling instructions
- **Phase Diagrams –**
  - Product, if used "as is." If product is always diluted or used in conjunction with another deicing chemical, the phase diagram for the product alone is not required.
  - If the chemical is intended to be mixed with another product or must be diluted to use, a phase diagram must be provided for the recommended dilution or mix with a DOT "base" chemical, i.e., rock salt, salt brine, calcium chloride or abrasives. (Intent is to assure that the phase diagram provided represents meaningful data in a real world situation). Suppliers may provide phase diagrams for more than one recommended mixes or dilutions, but it is not required.
- **MSDS sheet**
- **Chemical Composition –**
  - Provide a statement listing all elemental ingredients and the percentage of each ingredient included in the product and/or the patent number.
  - If product is to be mixed with another chemical, provide complete chemical composition of the product when mixed as recommended with a DOT "base" chemical
- **Sample –** Provide a one gallon sample each of liquid chemical or 5lbs of dry material, for lab testing. If product is to be diluted or mixed with another chemical for use, provide complete instructions for recommended dilution and/or mix, as the produce is recommended for use.

If the product complies with the pre-qualification criteria (the exact criteria are yet to be established – in the short term, Office of Maintenance personnel will review the pre-qualification materials. Any "red flags" will require committee consideration on whether to continue evaluation.

If pre-qualification criteria are fully met the sample chemicals will undergo lab testing at an independent lab for testing to verify that the new product complies with the claims of the manufacturer and if the chemical has qualities that would be worthwhile to field test.

LAB TESTS

In the short term, the Materials Lab will be asked to perform the chemical composition testing, however, future committee work will further define and set criteria for tests performed by an independent lab.

An independent lab will conduct tests on the product alone, as well as one additional test if the product is to be diluted or mixed with another DOT "base" chemical

An independent lab will test for:

- Chemical composition
  - test for hazardous materials and materials that could be damaging to Iowa's roadways and structure infrastructure (as identified by Materials?)
  - verify that product is as presented in pre-qualification phase
  - "baseline" for future shipments
- Environmental Impact
- Friction Test
- Drying Time Test
- Performance Tests (the results of the research underway by Wilfrid Nixon, U of I, will establish testing protocol)

Upon completion of the lab tests, the Iowa Deicing Chemical Committee will evaluate the information supplied in the pre-qualification phase and the results of the lab tests. The committee will determine if the product should proceed to operational testing.

OPERATIONAL TEST

In order to fully assess the efficiency and usability of any deicing chemical or deicing chemical additive, an operational test will be performed by one or more Iowa DOT maintenance garages to determine how the product will perform in a real world setting in Iowa's environment.

The operational tests will be conducted at a facility that has

- A location that fits the needs of the particular test (adequate storage capacity, appropriate roadway, etc.)
- Proper equipment (or ability to modify equipment) to handle the needs of the test.
- The ability and willingness to provide documentation of test results in the form of observations**,** forms, photographs, videos, or other means required for the test.

Limited financial assistance to a testing garage to obtain some items to accommodate the testing may be available through the Snow and Ice Section of the Office of Maintenance.

The location conducting operational tests shall select both a test and control section. The test section will be treated with the product being evaluated. The control section (a section of roadway similar to that of the test section) will be treated with standard, non-experimental chemicals. Control section should as similar as possible to the test section in the following ways:

- Same direction of travel
- Same or similar surface type
- Similar traffic volume
- Close proximity to the test section
- Ability to accomplish treatments on both test & control sections in a similar time frame

The following general information shall be documented about each test and control section.

- Location of the test and control section
- Traffic count for test and control section
- Type of pavement and texture

The following specific information shall be documented about each test and control section for each application cycle.

- Date and time of application
- Product name
- Application rate. If product is diluted or mixed with another chemical, indicate percentage of each product (i.e., 50% Product X/50% water)
- Speed of application
- Application method
- Weather conditions
    - Pavement temps
    - Air temp
    - Relative humidity
    - Sky conditions
    - Wind speed and direction
    - Precipitation type and rate
- Description of the observed results of the application on both the test and control section

- Road conditions at the following intervals
  - When treatment applied
  - At intervals of XX minutes
  - End results
- Traffic behavior
- Other factors

Supplement observations with photos or video whenever possible

APPENDIX C. TEST RESULTS FOR FREEZING POINTS, ICE MELTING ABILITY, AND VISCOSITY

C.1 Eutectic Temperature & Ice Melting Ability Laboratory Tests on Deicer Combinations

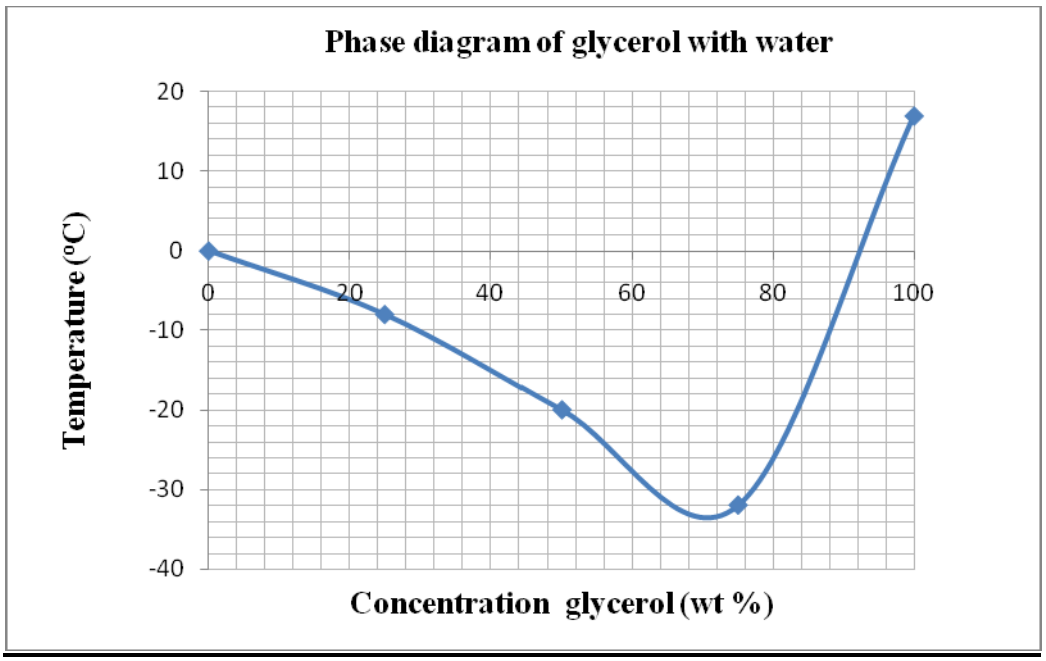
DOT Research Report
Kuldeep Wadhwa and John Verkade
Department of Chemistry
Iowa State University
June, 2009

We screened combination of NaCl or $MgCl_2$ with glycerol and other commercially available deicing agents to determine their eutectic temperature with water using phase diagrams, and we also determined the rate of ice melting of using the combinations listed below:

1. 100% glycerol (**A**)
2. 90% glycerol with 10% $MgCl_2$ (**B**)
3. 80% glycerol with 20% NaCl (**C**)
4. 90% Geomelt with 10% $MgCl_2$ (**D**)
5. 80% Geomelt with 20% NaCl (**E**)
6. 90% B-gone with 10% $MgCl_2$ (**F**)
7. 80% B-gone with 20% NaCl (**G**)
8. 50 % E310 + 50% glycerol (**H**)
9. 100% NaCl (**I**)
10. 5% solution of NaCl in water (**J**)
11. 40% E310 + 40% glycerol + 20% NaCl (**K**)
12. 50% glycerol + 50% $MgCl_2$ (**L**)

Phase diagram of glycerol (A) with water

Entry	Weight of Glycerol (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-8
2	50	50	-20
3	75	25	-32
4	100	0	17

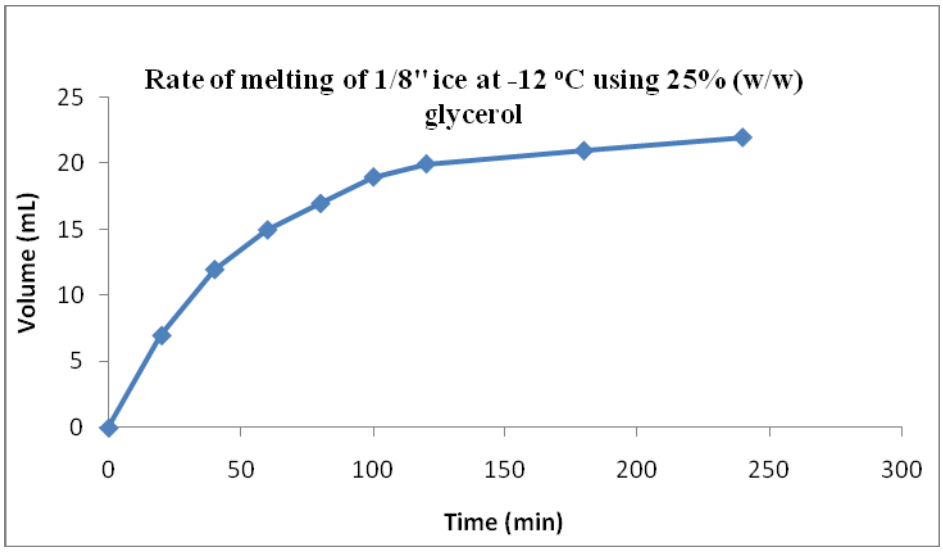


Eutectic Temperature = -34 ^{o}C
Eutectic Concentration = 70% (w/w)

Rate of melting of ice with glycerol as additive

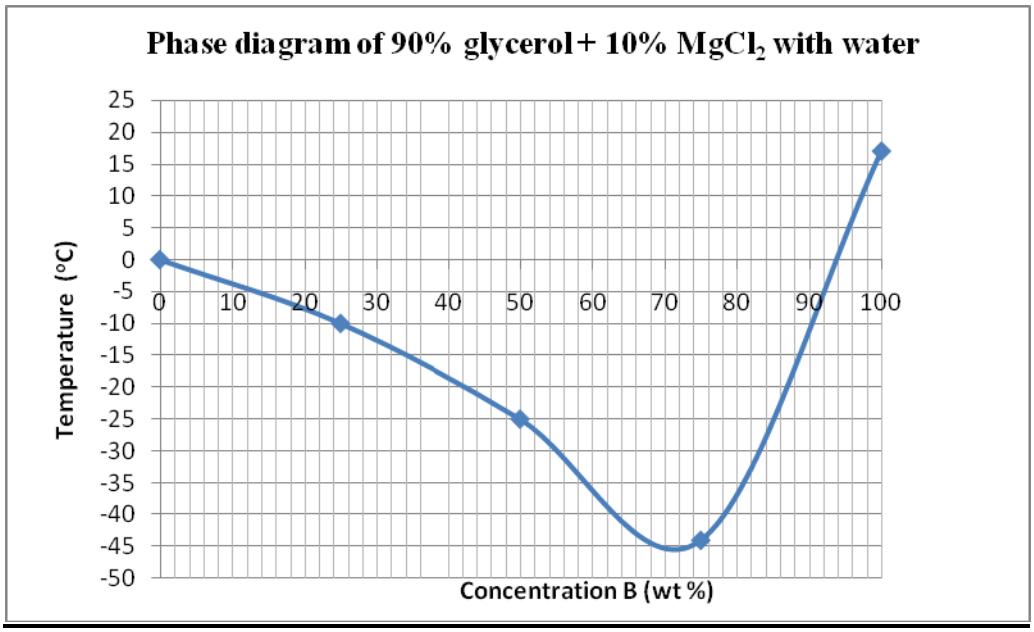
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch solid layer. To this was added 25% (w/w) of glycerol. The volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	7
3	40	12
4	60	15
5	80	17
6	100	19
7	120	20
8	180	21
9	240	22



Phase diagram of 90% glycerol + 10% $MgCl_2$ (B) with water

Entry	Weight of B (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-10
2	50	50	-25
3	75	25	-44
4	100	0	17

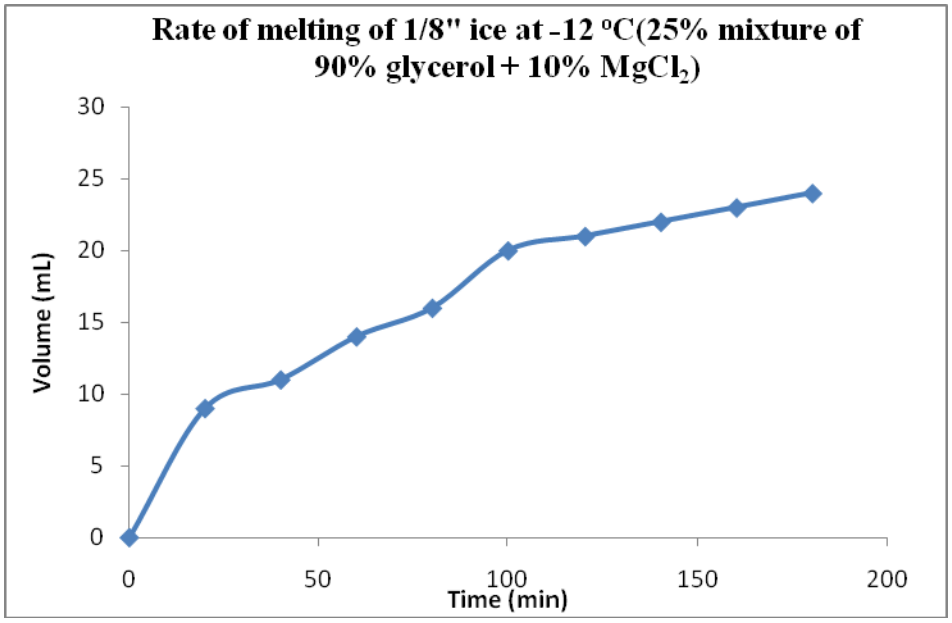


Eutectic Temperature = -45 ^oC
Eutectic Concentration = 72% (w/w)

Rate of melting of ice with 90% glycerol + 10% $MgCl_2$ (B) as additive

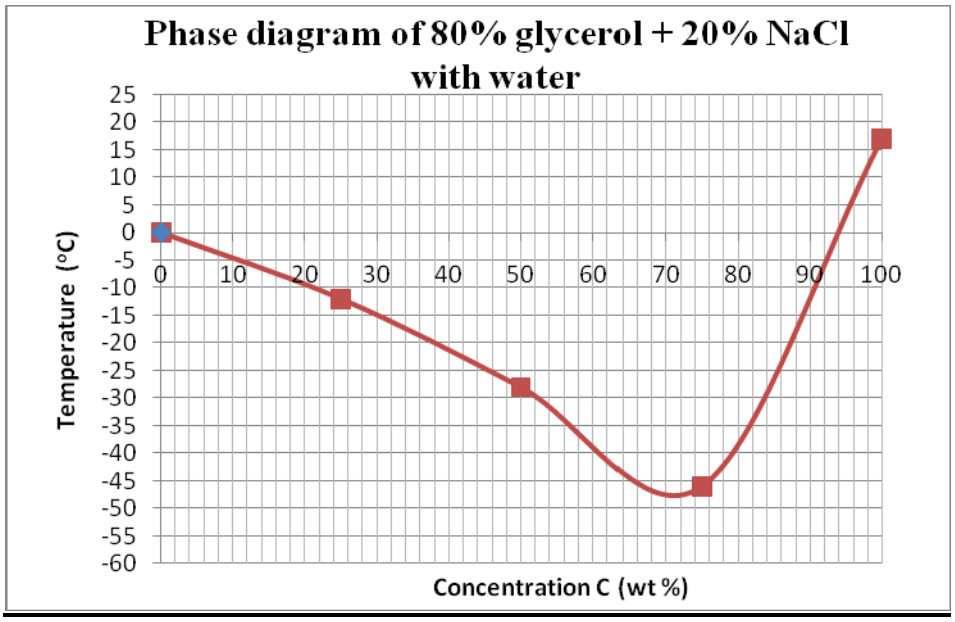
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^oC to form a 1/8 inch solid layer. To this was added 25% (w/w) of **B**. The volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	9.0
3	40	11.0
4	60	14.0
5	80	16.0
6	100	20.0
7	120	21.0
8	140	22.0
9	160	23.0
10	180	24.0
11	240	24.0



Phase diagram of 80% glycerol + 20% NaCl (C) with water

Entry	Weight of C (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-12
2	50	50	-26
3	75	25	-46
4	100	0	17

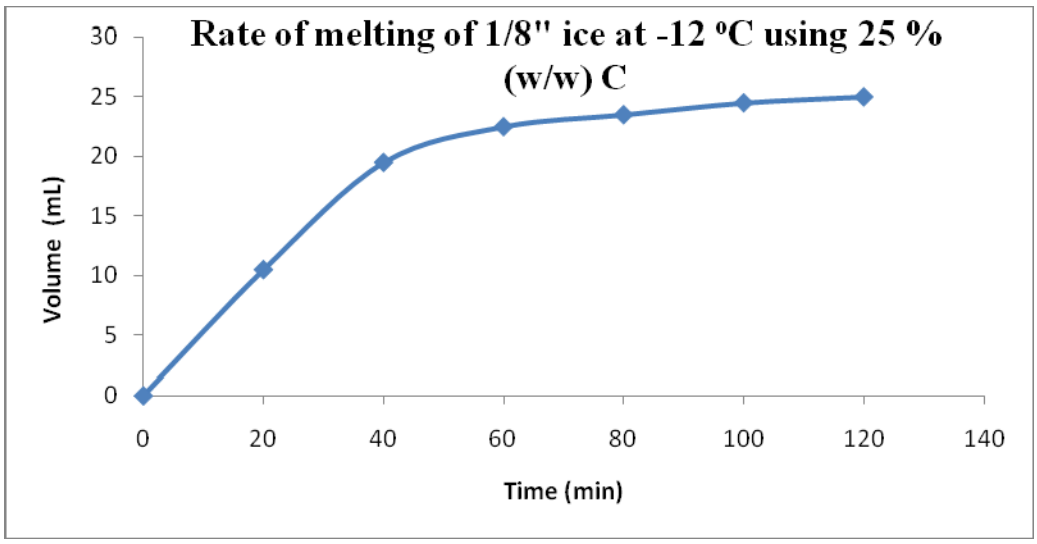


Eutectic Temperature = -48 ^{o}C
Eutectic Concentration = 72% (w/w)

Rate of melting of ice with 80% glycerol + 20% NaCl (C) as additive

Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch layer. To this was added 25 % (w/w) of **C** and the volume of water that melted was recorded at regular intervals of time.

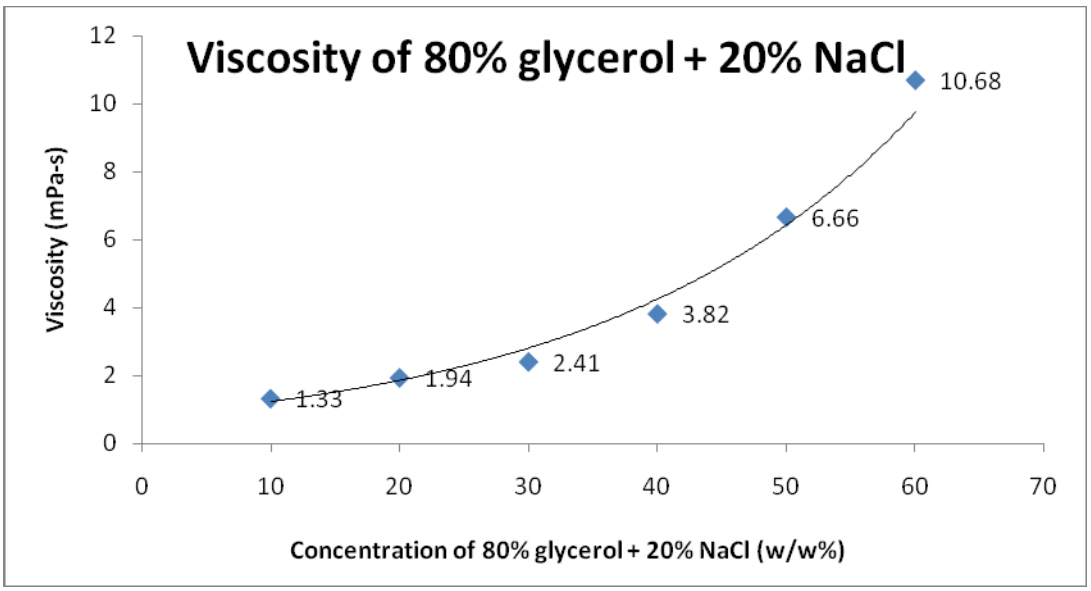
Entry	Time (min)	Volume (mL)
1	0	0
2	20	11.5
3	40	19.5
4	60	22.5
5	80	23.5
6	100	24.5
7	120	25



Determination of viscosity of glycerol + NaCl aq. solution

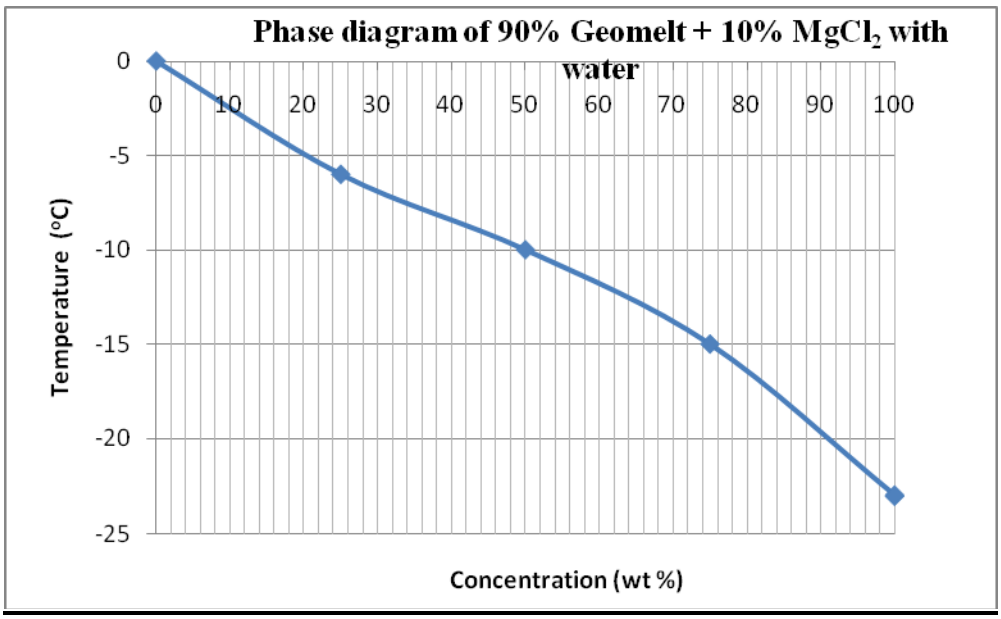
Experiment: Viscosity of aq. solution of glycerol + NaCl was measured using Ubbelohde viscometer using a standard procedure. The value of viscosity for various concentrations of 80% glycerol + 20% NaCl is listed in the table below.

Entry	Concentration of 80% Glycerol + 20% NaCl (w/w%)	Time (s)	Density (g/mL)	Viscosity (mPa-s)
1	10	1278	1	1.33
2	20	1759	1.06	1.94
3	30	2082	1.11	2.41
4	40	3242	1.13	3.82
5	50	5477	1.15	6.66
6	60	8465	1.21	10.68



Phase diagram of 90% Geomelt + 10% $MgCl_2$ (D) with water

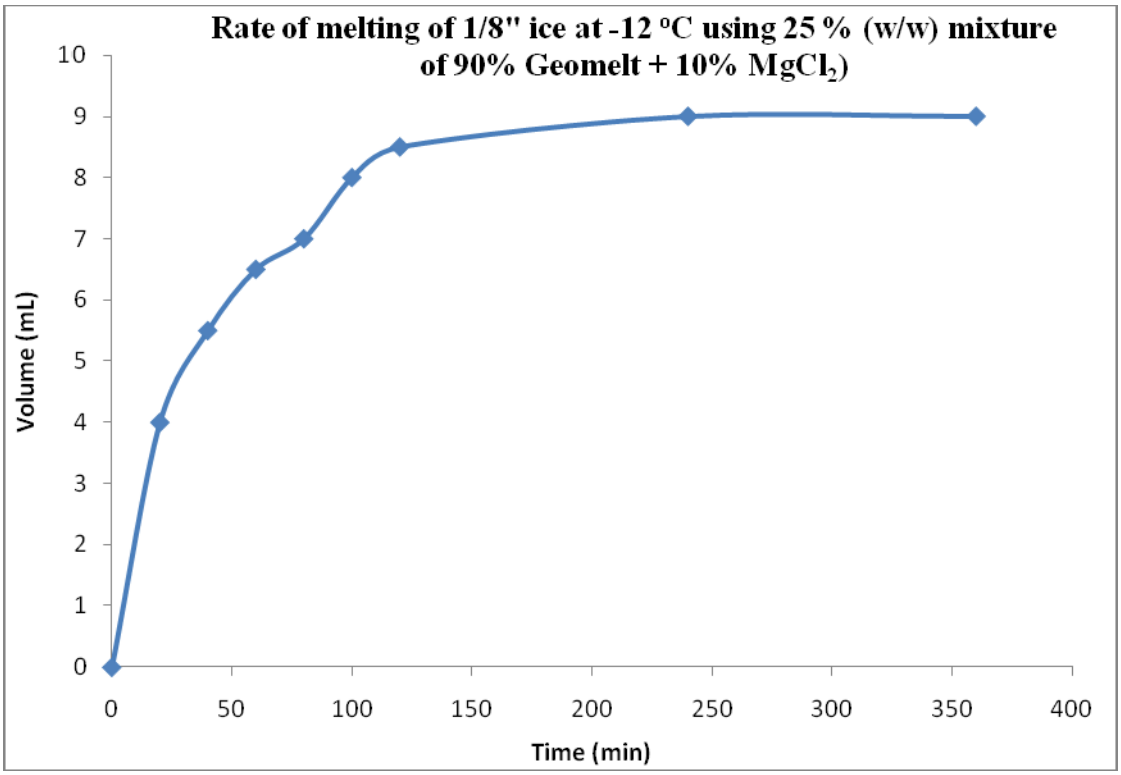
Entry	Weight of D (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-6
2	50	50	-10
3	75	25	-15
4	100	0	-23



Rate of melting of ice with 90% Geomelt + 10% $MgCl_2$ (D) as additive

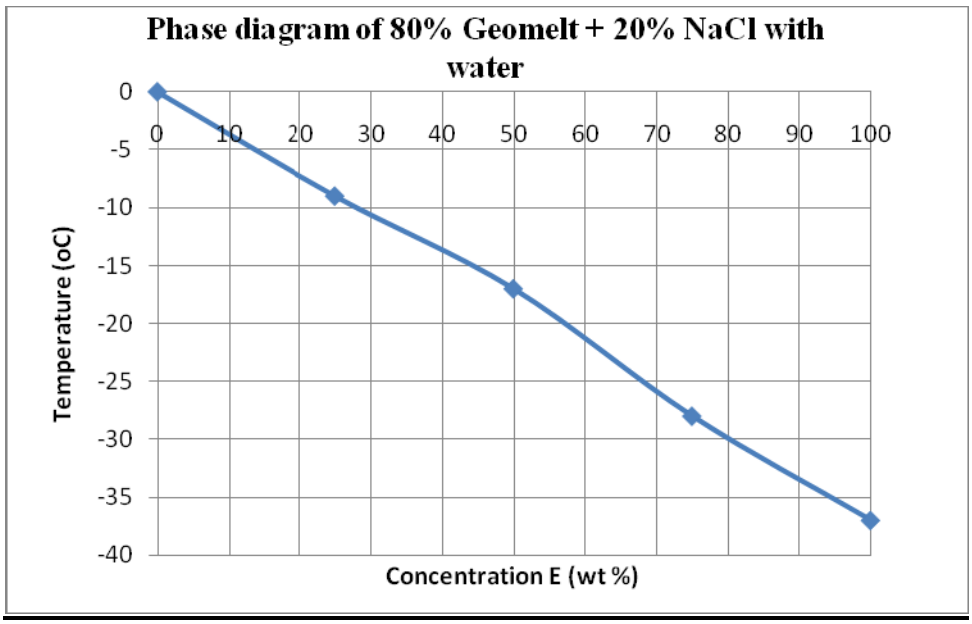
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^oC to form a 1/8 inch solid layer. To this was added 25 % (w/w) of **D** and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	4.0
3	40	5.5
4	60	6.5
5	80	7.0
6	100	8
7	120	8.5
8	360	9
9	480	9



Phase diagram of 80% Geomelt + 20% NaCl (E) with water

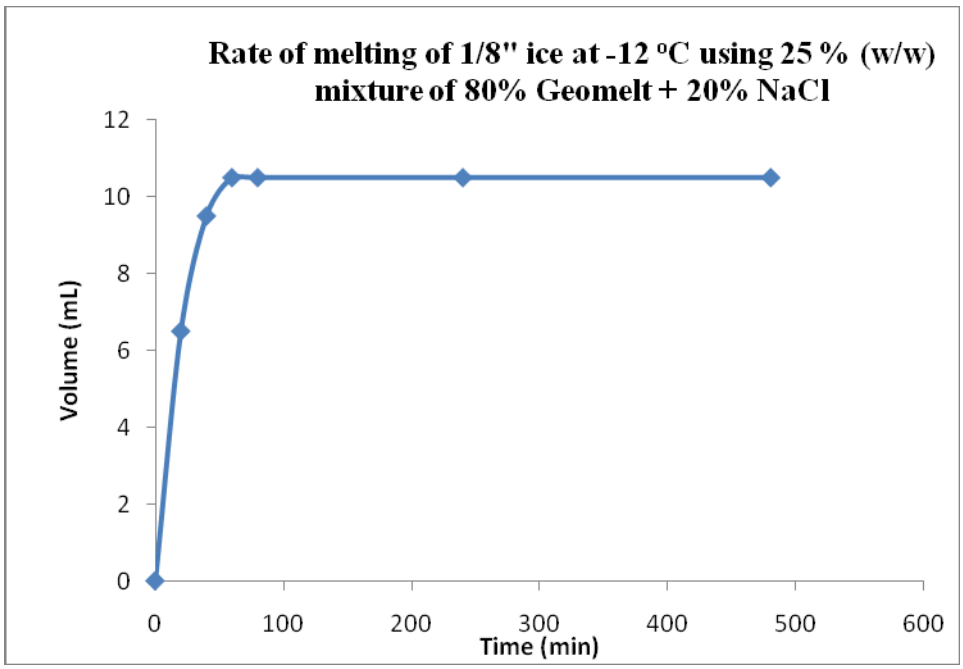
Entry	Weight of D (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-9
2	50	50	-17
3	75	25	-28
4	100	0	-37



Rate of melting of ice with 80% Geomelt + 20% $NaCl_2$ (E) as additive

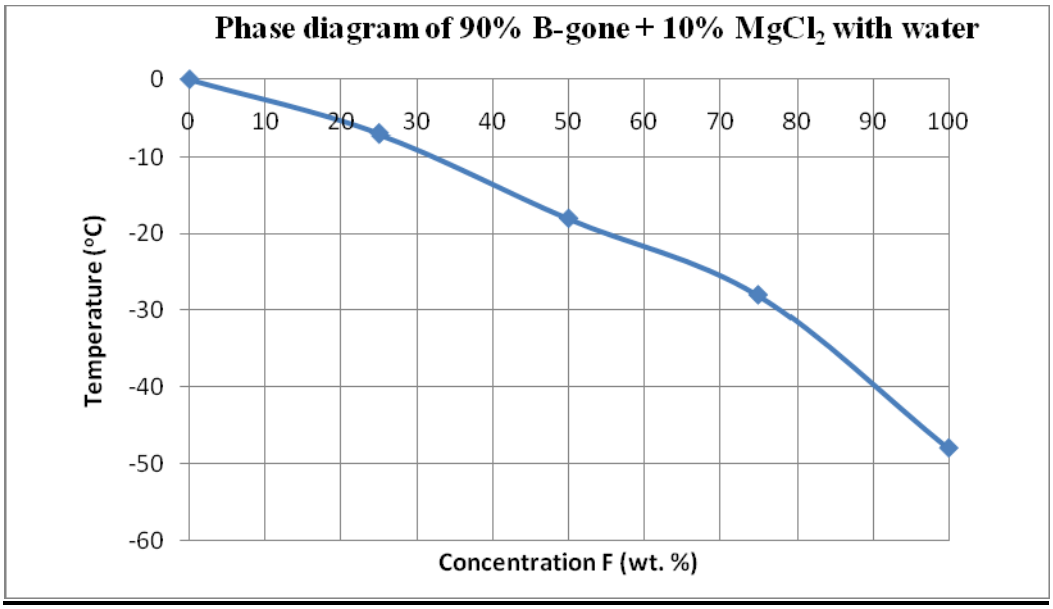
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch solid layer. To this was added 25 % (w/w) of **E** and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	6.5
3	40	9.5
4	60	10.5
5	80	10.5
6	240	10.5
7	480	10.5



Phase diagram of 90% B-gone + 10% $MgCl_2$ (F) with water

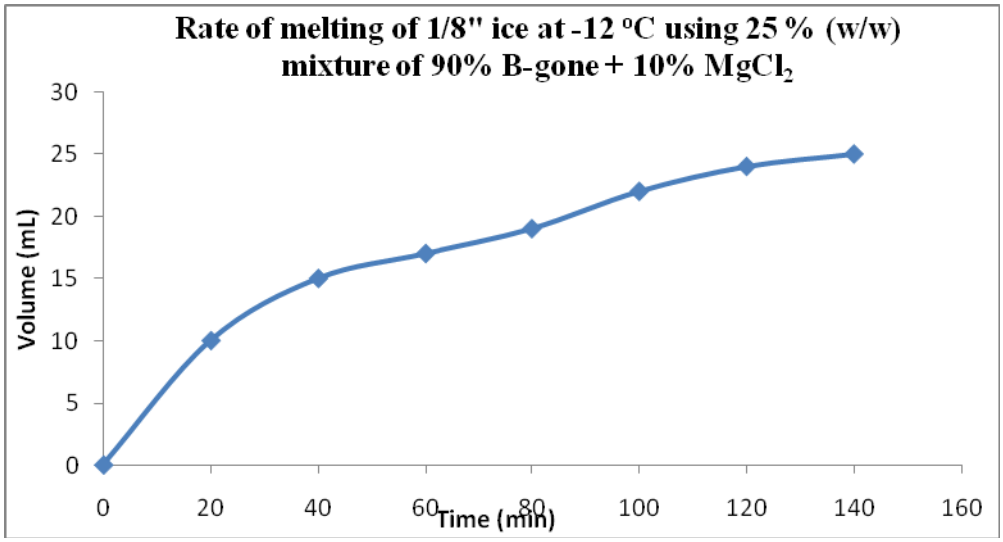
Entry	Weight of D (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-7
2	50	50	-18
3	75	25	-28
4	100	0	-48



Rate of melting of ice with 90% B-gone + 10% $MgCl_2$ (F) as additive

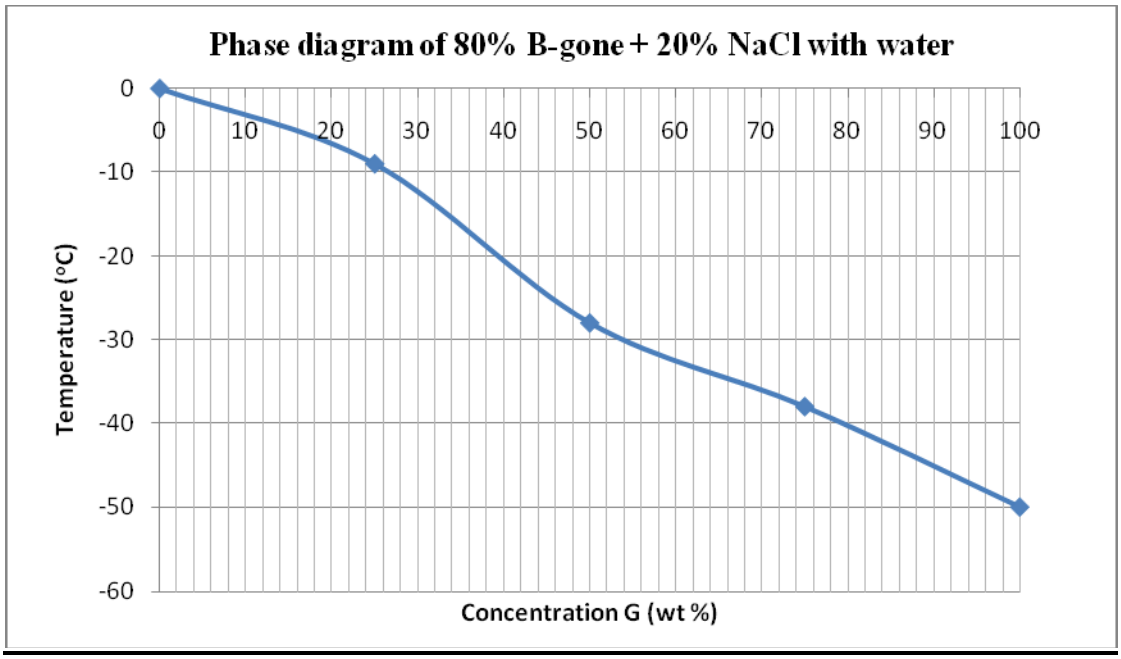
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^oC to form a 1/8 inch solid layer. To this was added 25 % (w/w) of **F** and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	10
3	40	15
4	60	17
5	80	19
6	100	22
7	120	24
8	140	25



Phase diagram of 80% B-gone + 20% NaCl (G) with water

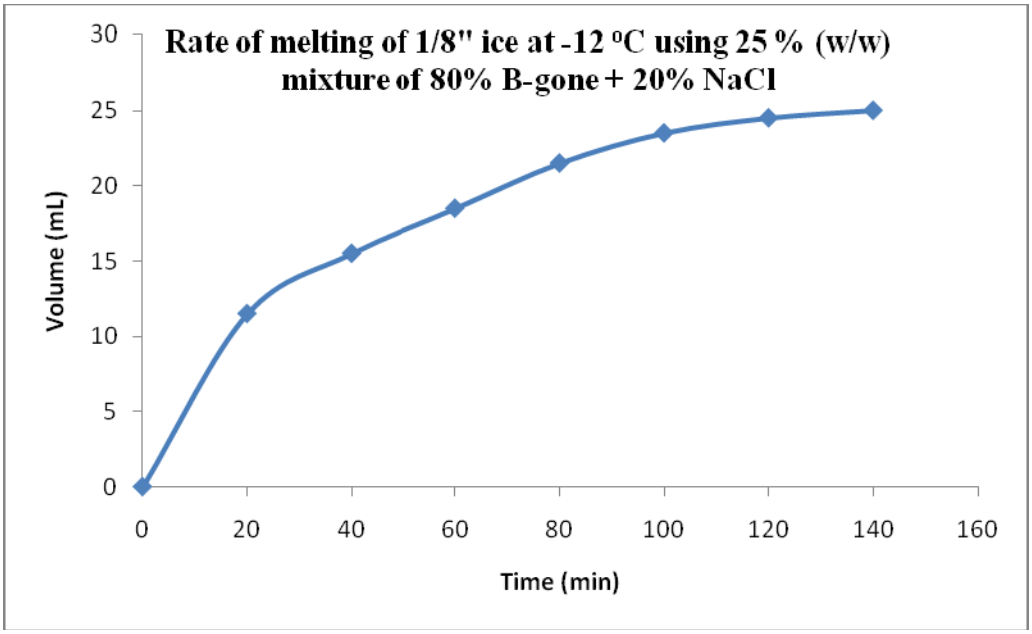
Entry	Weight of D (%)	Weight of Water (%)	Freezing Point (^oC)
1	25	75	-9
2	50	50	-28
3	75	25	-38
4	100	0	>-50



Rate of melting of ice with 80% B-gone + 20% $NaCl_2$ (G) as additive

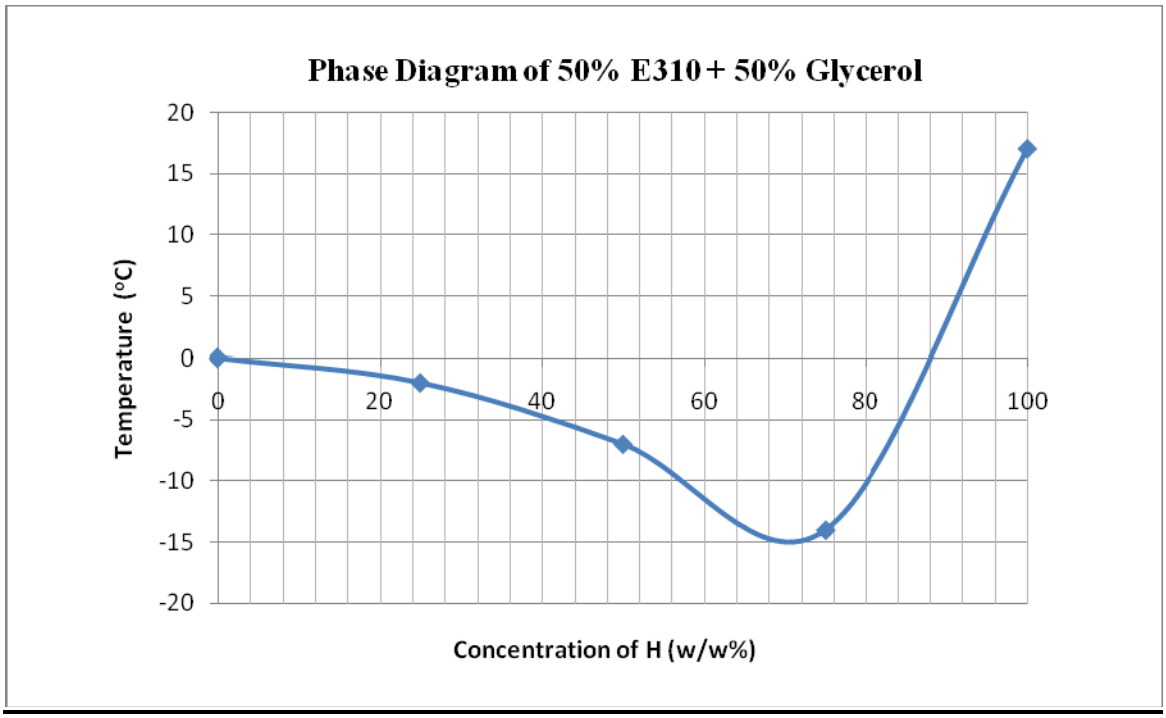
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch solid layer. To this was added 25 % (w/w) of **G** and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	11.5
3	40	15.5
4	60	18.5
5	80	21.5
6	100	23.5
7	120	24.5
8	140	25.0



Phase diagram of 50% E310 + 50% glycerol (H) with water

Entry	Weight of H (%)	Weight of Water (%)	Freezing Point (^{o}C)
1	25	75	-2.0
2	50	50	-7.0
3	75	25	-14.0
4	100	0	17.0

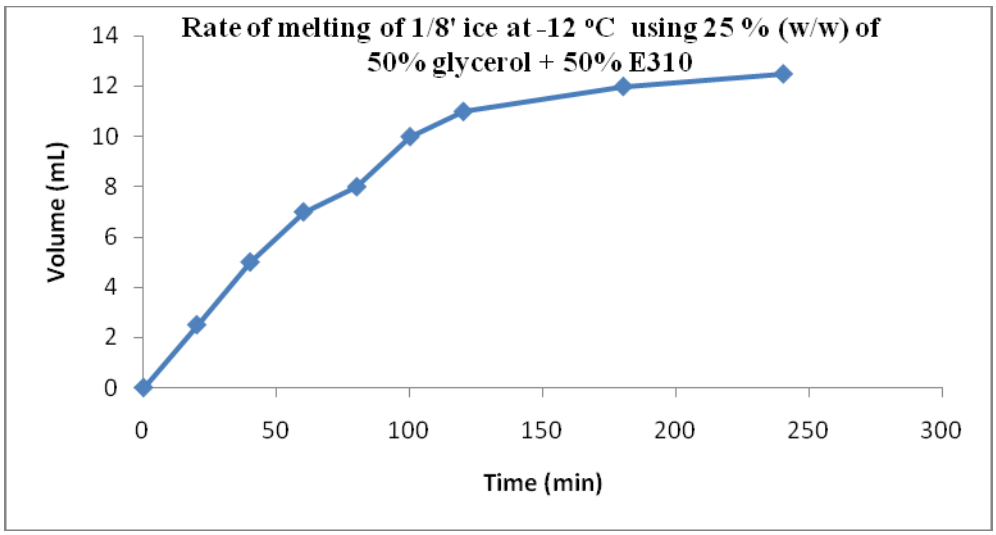


Eutectic Temperature = -15 °C
Eutectic Concentration = 70% (w/w)

Rate of melting of ice with 25% of H as additive

Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 °C to form a 1/8 inch layer. To this was added 25% (w/w) of **H** and the volume of water that melted was recorded at regular intervals of time.

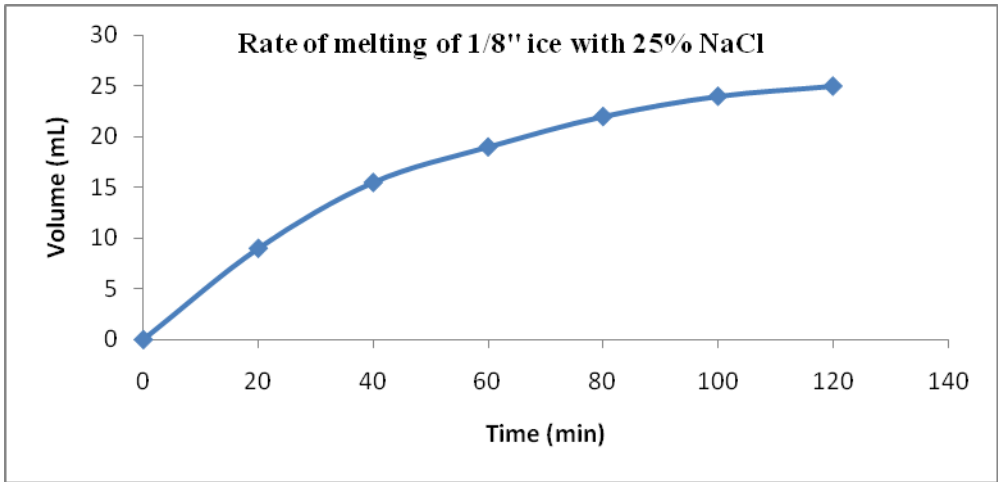
Entry	Time (min)	Volume (mL)
1	0	0
2	20	2.5
3	40	5.0
4	60	7.0
5	80	8.0
6	100	10.0
7	120	11.0
8	180	12.0
9	240	12.5



Rate of melting of ice with 25% NaCl as additive

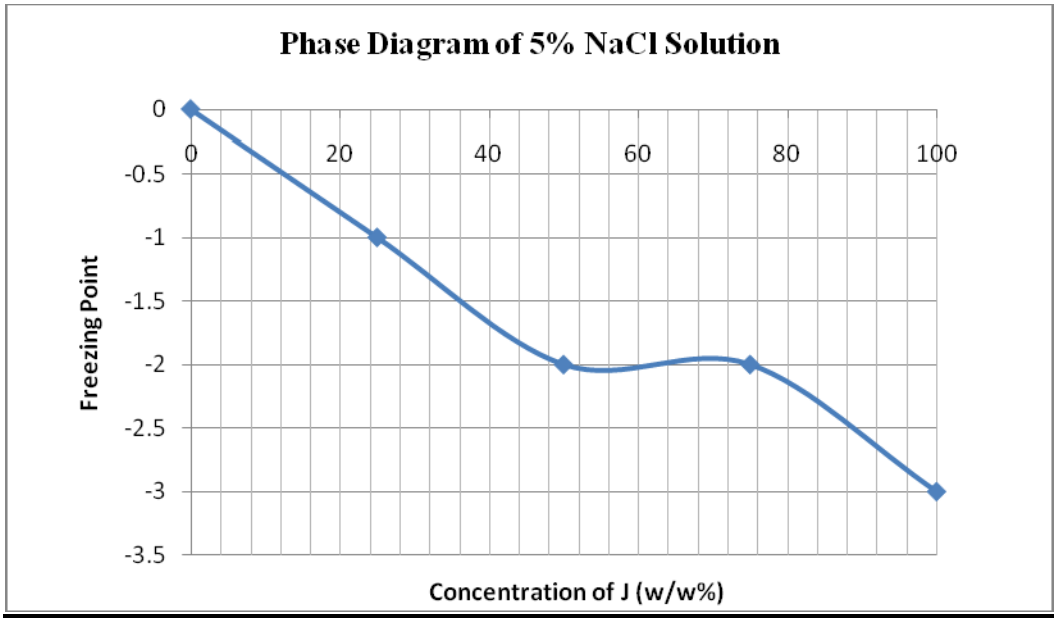
Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch layer. To this was added 25 % (w/w) of NaCl (**I**) and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	9.0
3	40	15.5
4	60	19.0
5	80	22.0
6	100	24.0
7	120	25.0



Phase diagram of 5% NaCl (J) with water

Entry	Weight of J (%)	Weight of Water (%)	Freezing Point (^{o}C)
1	25	75	-1.0
2	50	50	-2.0
3	75	25	-2.0
4	100	0	-3.0



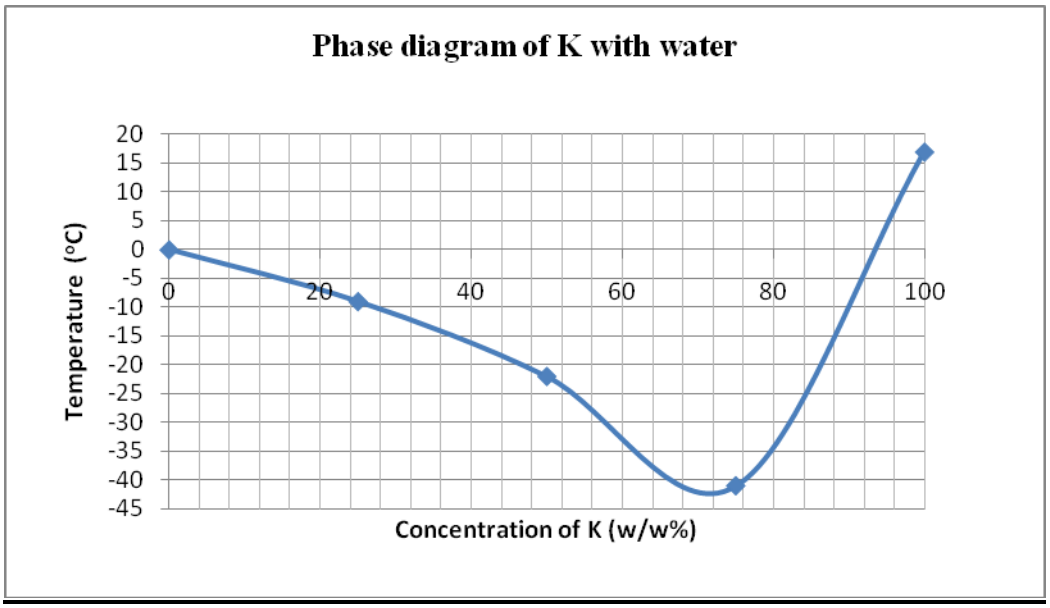
Rate of melting of ice with 25% of J as additive

Experiment #1: 25 ml water was taken in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch layer. To this was added 25% (w/w) of **J** and the volume of water that melted was recorded at regular intervals of time.

Observation: 25% (w/w) was ineffective in melting the layer of 1/8" ice at -12 ^{o}C.

Phase diagram of 40% E310 + 40% glycerol + 20% NaCl (K) with water

Entry	Weight of K (%)	Weight of Water (%)	Freezing Point (^{o}C)
1	25	75	-9
2	50	50	-22
3	75	25	-41
4	100	0	17

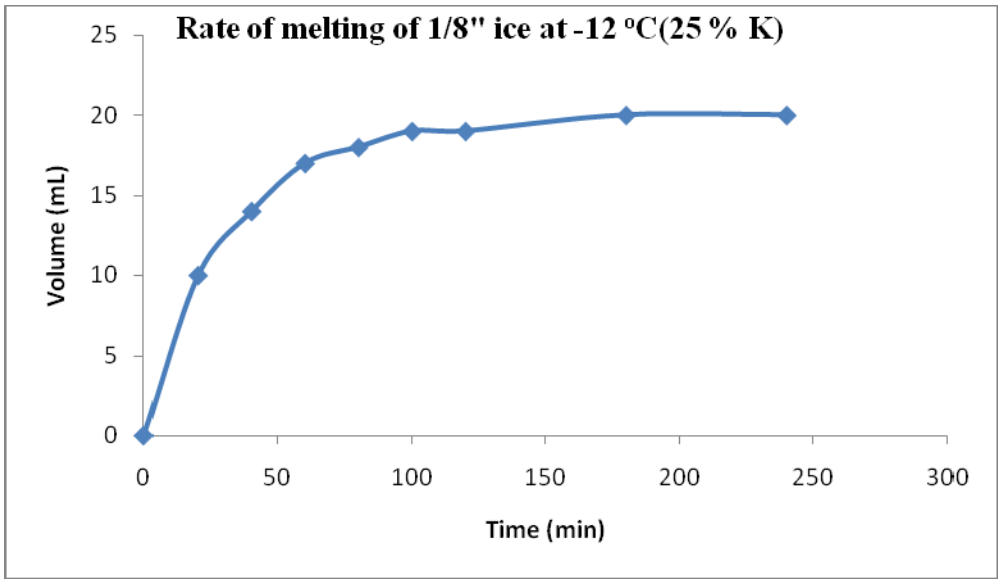


Eutectic Temperature = -42 ^{o}C
Eutectic Concentration = 72% (w/w)

Rate of melting of ice with K as additive

Experiment #1: 25 ml water was taken in a flat bottom dish and was frozen in a constant temperature bath at -12 ^{o}C to form a 1/8 inch layer. To this was added 25 % (w/w) of **K** and the volume of water that melted was recorded at regular intervals of time.

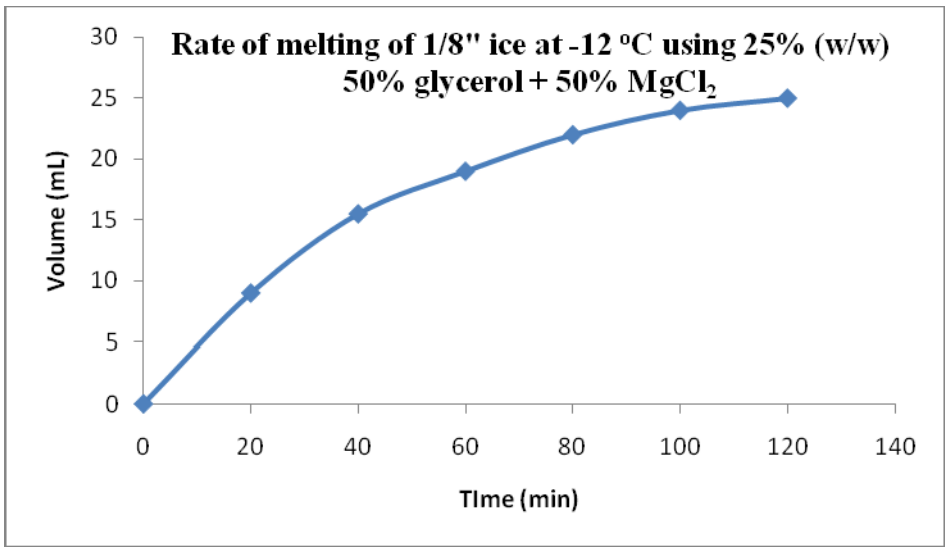
Entry	Time (min)	Volume (mL)
1	0	0
2	20	10.0
3	40	14.0
4	60	17.0
5	80	18.0
6	100	19.0
7	120	19.0
8	180	20.0
9	240	20.0



Rate of melting of ice with 50% glycerol + 50% $MgCl_2$ (L) as additive

Experiment #1: 25 ml water was placed in a flat bottom dish and was frozen in a constant temperature bath at -12 °C to form a 1/8 inch layer. To this was added 25% (w/w) of **L** and the volume of water that melted was recorded at regular intervals of time.

Entry	Time (min)	Volume (mL)
1	0	0
2	20	9.0
3	40	15.5
4	60	19.0
5	80	22.0
6	100	24.0
7	120	25.0



Conclusions

1. We found that the combinations listed below showed comparable performance in the tests we performed for the rate of melting of ice under our laboratory conditions.
   (a) 90% glycerol + 10% $MgCl_2$ (**B**)
   (b) 80% glycerol + 20% NaCl (**C**)
   (c) 90% B-gone + 10% $MgCl_2$ (**F**)
   (d) 80% B-gone + 20% NaCl (**G**)
   (e) 100% NaCl (**I**)
   (f) 50% glycerol + 50% $MgCl_2$
2. The combination of 50% glycerol + 50%$MgCl_2$ was slightly better then commercially available B-gone. It took 120 min to melt the layer of ice for 50% glycerol + 50% $MgCl_2$, whereas B-Gone (80% $MgCl_2$ + 20% molasses) with $MgCl_2$ and NaCl as additive took 140 min to melt the same thickness of ice layer at the same temperature
3. It was found that 80% glycerol + 20% NaCl was the best performer among the friction tests carried out by Dr. Rangan. We discovered that among all the samples friction tested, 50% glycerol + 50% $MgCl_2$ was equally effective as 100% NaCl. We therefore propose that the use of 50% glycerol + 50% $MgCl_2$ might prove to be even better in frictional properties on roads than the 80% glycerol + 20% NaCl, due to the higher salt concentration in the 50%/50% mixture, and will be less corrosive compared with 100% rock salt.
4. The commercially available deicer Geomelt did not function as well when compared with the combinations tested in our laboratory.

The biodegradability of glycerol, its high solubility in water, its odor-free character and its colorless appearance combine to make it a better choice when compared with commercially available deicers such as B-gone and Geomelt which are dark in color and have a strong unpleasant odor.

C.2 Viscosity Tests on Selected Ag-based Deicer Combination

Entry	Concentration of 80% Glycerol + 20% NaCl (w/w%)	Time (s)	Density (g/mL)	Viscosity (mPa-s)
1	10	1278	1	1.33
2	20	1759	1.06	1.94
3	30	2082	1.11	2.41
4	40	3242	1.13	3.82
5	50	5477	1.15	6.66
6	60	8465	1.21	10.68